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IS CHEMICAL ACTION AFFECTED BY MAGNETISM?

BY MORRIS LOEB.

The close relationship between electricity and chemical affinity on the one hand, and that between electricity and magnetism on the other, have naturally raised the question whether any relation can be traced between affinity and magnetism.

This question was the subject of numerous investigations during the entire first half of this century,[1] but appears to have dropped out of sight, until Prof. Remsen,[2] in 1882, again attracted attention to it by the interesting observation that, from a solution of the sulphate, copper is unequally deposited upon the armature of a horse-shoe magnet. Other experiments by Messrs. Nichols and Franklin,[3] and Messrs. Rowland and Bell,[4] have also borne relation to this question. I have nevertheless ventured to approach the subject from a new side, with the conviction that all of these investigations introduce phenomena which tend to obscure the point at issue, *i. e.* the effect of magnetism upon the chemical reaction itself. This will be made clear by an analysis of the principles upon which these investigations have been conducted: they can be divided into four categories.

The earliest experiments regarded the rusting of bar magnets; and the most trustworthy observers appear to invalidate the assertion of a few, that magnetised iron differs from the non-

[1] For full literature see E. Wartmann: Phil. Mag. **30**, 266. [2] This Journal **3**, 137.
[3] Am. J. Sci. **34**, 419; **35**, 290. [4] Phil. Mag. **26**, 105.

magnetised metal in this respect, or that the north and south poles show dissimilar behavior. The experiments were naturally crude, and a positive result, were it admitted, would obviously have been due to a polarised arrangement of the molecules, rather than to variations in chemical affinity.

Next came the crystallisation of salts or metals from a solution, within and without a magnet field. Quite a number of observers appear to have found that the *direction* of growth, either of the crystals themselves or of the clusters which they form, can be affected by the presence of a magnetic field, even though the substance be a diamagnetic. But what is there in this that involves a modification of chemical action? The quantity of deposit has not been observed to be altered by the magnet; the physical arrangement of the molecules during crystallisation is always governed by directive forces having no connection with affinity, and to the ordinary ones is now superimposed the polarising influence of the magnet.

A different principle is involved in Remsen's experiments, for they depend upon the removal of particles from a magnetised mass of iron, and the substitution therefor of faintly-magnetic copper. The explanation of Messrs. Rowland and Bell must appear highly plausible, that the resistance to such removal must protect the more highly magnetised points from reaction, so long as there are places where the iron can be more readily dissolved. We have here a purely mechanical reason for the localisation of the reaction, in a non-uniform field. That the *total* amount of reaction would not be affected we may infer from a recent experiment by Fossati,[1] in which he shows that the weight of iron precipitated from a solution by zinc is not affected by the presence of a strong magnetic field.

Apparently inconsistent with the protection-hypothesis are the observations of Messrs. Nichols and Franklin, which show that iron which has become passive through the action of strong nitric acid, suddenly regains its activity when introduced into a magnetic field. One might be tempted to ascribe this to the exposure of fresh surfaces, owing to the rearrangement of the molecules during magnetisation; but since the investigators have reason to seek the cause in the induction of local electric currents by the magnet,

[1] Bolletino dell' Elettricista, 1890. I quote from Wiedemann's Beiblätter, 1890, p. 1010, which alone is at my disposal.

we may assign this phenomenon to the fourth category, that of galvanic action in the magnetic field. To my knowledge, Messrs. Nichols and Franklin were the first to experiment upon the effect of an unequal magnetic field upon an electrolyte: the movement of the paramagnetic salt to the interior portions of the field, and the inequality of electric potential consequent upon the variation of concentration, were proved, as might be expected. We have, then, this effect, as well as that of the Faradic induction, to account for any irregularities which the galvanoscope might indicate, when a solution undergoing electrolysis was also subjected to magnetic influence. Messrs. Nichols and Franklin do ascribe their observations to this cause, and see no reason to introduce a supposed change of the chemical conditions.

I fail to see any significance in the experiment of placing one of two gas-voltameters, or one of two cells containing an iron solution,[1] in a magnetic field, and looking for a difference in the amount of decomposition when a current is passed through the couple in series. Surely no such result could be expected in the face of the universally acknowledged Law of Faraday, unless, indeed, a magnetic field were imagined to alter the quantivalence of the elements.

To sum up: all experiments hitherto made have introduced non-chemical phenomena, due either to the inequalities of the magnetic field, or to the physical heterogeneity of the reacting system, or to both of these causes at once. It was my wish to study the effect of magnetism upon chemical reaction where the system remained homogeneous throughout, and where the field of stress was practically homogeneous. Such conditions can be realised by observing the speed of some reaction which does not involve solids, in the presence of a magnet, and, again, when there is no magnetic effect, provided the magnetic properties of the system could be altered by the reaction. In the same manner as an electric system is affected by its approach to or removal from a magnetic field, we might suppose that a reaction which made a system more or less amenable to magnetic action, might show evidence of acceleration or retardation by the magnetic force. If this effect were appreciable, the relation between magnetic force and affinity would be established, and data could be obtained for calculating the real value of magnetisation.

[1] Fossati.

My results, however, have been negative, and I am led to believe that no such relation exists, unless it be so slight that my means of observation have been inadequate. Being confident, however, that my method has been of no lower order of delicacy than those hitherto employed in connection with the subject, I do not hesitate to assert that the interesting effects which have been noted are not due to a variation of affinity or of chemical reaction in its strictest sense. For this reason I herewith present my results.—

The choice of material for my investigation was rather limited: of all compounds, the salts of the iron group alone yield markedly paramagnetic solutions; furthermore, Wiedemann has shown that the ordinary form of reaction between salts does not affect the total magnetism of the system, so long as it involves merely an interchange of acids. But there is a marked change when the constitution of one of the ingredients is altered: the atomic magnetism of trivalent iron is 25 per cent. greater than that of the same element in the ferrous state. I resolved, therefore, to study the effect of magnetism upon the speed of oxidation and reduction of iron salts in solution by reagents which showed but a feeble magnetism by themselves.

Two such reactions have already been studied under ordinary conditions, and, inasmuch as the methods employed seemed admirably suited to my purpose, I have followed them in this investigation.

Dr. J. J. Hood[1] determined the speed of the reaction

$$6FeSO_4 + KClO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + KCl + 3H_2O,$$

by estimating volumetrically with permanganate the amount of ferrous salt remaining unaffected at different stages of the process.

Meyerhoffer[2] gives one series of observations upon the reaction

$$2HI + 2FeCl_3 = I_2 + 2FeCl_2 + 2HCl,$$

in which case the iodine which had been set free could be determined with starch paste and sodic thiosulphate.

Oxidation of a Ferrous Salt.

I had at my disposal a large Ruhmkorff electro-magnet, with cylindrical iron cores ten inches long and three inches thick.

[1] Phil. Mag. [5] **6**, 371; **8**, 121; **13**, 419. [2] Ztschr. phys. Chem. **2**, 597.

With the poles three inches apart, and with a current from ten storage cells, the intensity of the magnetic field was roughly determined at 10,000 c. g. s. per square-centimeter. For my supply of electricity I am indebted to the kindness of the director of the Physical Laboratory, Prof. A. A. Michelson. While ten cells were usually employed, I sometimes was enabled to use double that number, and in several instances obtained the current directly from the dynamo, employing as full a current as the apparatus would safely bear. Because the results were always virtually identical, no pains were taken to determine the exact strength of the magnetic field, but 18,000 c. g. s. is a low estimate of the maximum reached.

The axes of the cores being horizontal, a prismatic battery cell, 2½x6x6 inches, was placed between the poles to serve as a bath of constant temperature. It was therefore protected from direct contact with the poles by thin layers of cotton batting, and was traversed by a rapid current of water from a reservoir whose contents were kept within 0.1° C. of the desired temperature.

The solutions were contained in a sort of pocket-flask of 100 cc. capacity, an inch thick, and having two flat sides of circular outline three inches in diameter. This flask was suspended in the bath in such a manner as to be just between the poles of the magnet. The solutions which were not to be subjected to the influence of the magnet were contained in a precisely similar flask, and the water-bath in which this was placed was fed by the overflow from the first mentioned one. Where it was not feasible to observe the two reactions at the same time, especial care was taken to keep the temperature constant.

The following solutions were employed: a $\frac{1}{3}$-molecular solution of potassium chlorate, a $\frac{1}{2}$-molecular solution of sulphuric acid, a $\frac{1}{2}$-molecular solution of ferrous sulphate, a solution of potassium permanganate of which 12.5 cc. corresponded to 1 cc. of the iron solution. The latter was made from crystallised ferrous sulphate, with a little sulphuric acid and an excess of metallic iron, so that it was very nearly neutral.

Proper volumes of the chlorate and the acid solutions having been run into the flask and sufficient water to make the volume 80 cc., the solution was allowed to acquire the temperature of the water-bath. Thereupon 20 cc. of the ferrous sulphate solution, which had been brought to the same temperature, were added

rapidly, the flask was vigorously shaken, and at once replaced in the water-bath. If the magnet was to be employed, its electric circuit was closed at this time. After the expiration of a few minutes, 10 cc. were withdrawn from the flask by means of a pipette, and were quickly run into a large quantity of cold water contained in a porcelain dish, the time being noted when the pipette was emptied. The titration was then executed as rapidly as possible. This operation was repeated at suitable intervals, until the solution was exhausted or external conditions prevented a continuation of the observation. Where two reactions were to be observed together, the second solution was mixed ten minutes after the first, the same interval being preserved, as nearly as might be, throughout. Owing to the weakness of the permanganate solution and to varying conditions of illumination, my titrations have a probable error of fully $\frac{1}{20}$—$\frac{1}{15}$ cc., but this is in no unfavorable proportion to the observed values; in cases of over-coloration I rejected the result, rather than titrate back with another solution.

The reaction has been proved by Hood to be subject to the law

$$\frac{dx}{dt} = C(A-x)(B-x),$$

where $x =$ the amount of substance changed, $t =$ time elapsed, A and B represent the original quantities of ferrous sulphate and chlorate respectively, and C is a coefficient depending on external circumstances.

As equivalent quantities of A and B were used,

$$\frac{dx}{dt} = C(A-x)^2.$$

Integrating, $$\frac{1}{A-x} = Ct + \text{constant}.$$

Calculating this constant from the initial conditions $t = 0$, $x = 0$, constant $= \frac{1}{A}$, and consequently

$$C = \frac{1}{At} \cdot \frac{x}{A-x}.$$

A is the amount of permanganate required at the first titration, and $A-x$ represents the amount of each subsequent one, after the lapse of t minutes. We possess all the data for calculating C. This coefficient has been shown by Hood to depend upon the temperature, to be augmented by the presence of free

acid, and diminished by the presence of neutral salts not participating in the reaction. It is consequently decreasing continually during the reaction, most noticeably, however, toward the end. Furthermore, if magnetism is of influence, the values of C must show it. In order to eliminate the other influences, I have sought to take the samples from corresponding solutions at the same intervals of time, and have varied the conditions somewhat by changing the temperatures as well as the amounts of sulphuric acid present in different series.[1] It will be seen that, while there is considerable variation between individual determinations, these variations are no greater between analogous samples of two corresponding series than between two succeeding samples of the same series. Further, the means of the whole series agree well with each other. The tables which I subjoin are selected, solely with reference to their general reliability, from a larger mass of material, all of which gave analogous results. While the effect of magnetism should produce acceleration, the variations of C from that of the non-magnetic reaction are negative quite as frequently as positive.

Series I.—$KClO_3 + 6FeSO_4 + 3H_2SO_4$. Temperature, 10.2°.

Series II.—Same conditions, in magnetic field (10 cells).

t.		$A-x$.		C.	
I.	II.	I.	II.	I.	II.
0	0	24.38	24.26	...	...
30.25	29.75	22.78	22.88	.049524	.048357
105	104.25	20.22	20.28	8050	7940
155.17	154.86	18.71	18.68	8011	7951
210	210	17.49	17.27	7695	7942
241	241.33	16.82	16.79	7546	7599
305.25	305.5	15.64	15.53	7491	7584
		Mean, ...		.048051	.047895
		Mean of last five, .		.047758	.047803

Series III.—Same relation, $KClO_3 : FeSO_4$; great excess H_2SO_4. Temperature, 18.7°.

Series IV.—Same as III, but with magnet (20 cells).

Series V.—Same as III, but with magnet (dynamo).

[1] In this connection it may be interesting to note that this reaction is, according to my experiments, barely perceptible at 0° C.—a result which agrees closely with the limit set by Dr. Hood by extrapolation with his temperature-coefficient.

t.			*A* − *x.*			*C.*		
III.	IV.	V.	III.	IV.	V.	III.	IV.	V.
0	0	0	23.16	23 10	23.10	...	...	...
20	20	20.5	18.57	18.39	18.32	.0₂5335	.0₂5543	.0₂5509
40	40	40	15.33	15.45	15.41	5513	5358	5400
60	60	60	13.28	13.38	13.21	5353	5241	5401
80	80.5	80	11.71	11.58	11.42	5276	5348	5534
100	100.25	100	10.41	10.45	10.40	5288	5227	5286
120	120	120	9.38	lost.	9.45	5282	...	5211
139.75	130.75	140	8.72	8.99	8.54	5116	5197	5272
160.25	155	161	7.94	8.17	7.84	5164	5104	5233
					Mean,	.0₂5292	.0₂5288	.0₂5355

Reduction of Ferric Chloride.

The reaction $2HI + 2FeCl_3 = I_2 + 2FeCl_2 + 2HCl$, is not a simple one, being reversible, and furthermore accompanied by complicating bye-reactions. It seemed better to avoid all attempts to obtain the reaction-coefficients, and to make parallel experiments, with exactly the same time-intervals. If the magnetic force had any effect, this must be visible from the burette-readings.

The method used was exactly as before, but diluted solutions were employed to prevent the loss of free iodine. Equivalent quantities of hydriodic acid and ferric chloride were allowed to react in $\frac{1}{100}$-molecular solutions, and 10 cc. were taken out at a time and titrated with $\frac{1}{115}$-normal sodium thiosulphate solution. The determinations were very exact, and the corresponding burette-readings will be found to correspond so closely as to leave no doubt of the exact equality of speed within and without the magnetic field. I give all the series which were observed; in the second set, the reaction was carried as far as it would go—at least there was no more iodine liberated after $15\frac{3}{4}$ hours' standing.

Temperature, 17.8°.

Without Magnet.		With Magnet (dynamo).	
Time.	$Na_2S_2O_3$ required.	Time.	$Na_2S_2O_3$ required.
30.5	3.89	30.5	3.95
60	4.80	60	4.52
120	5.10	120	5.10
180	5.55	180	5.40
231	5.60	231	5.58

Same conditions.

Without Magnet.		With Magnet (dynamo).	
Time.	$Na_2S_2O_3$ required.	Time.	$Na_2S_2O_3$ required.
40	5.99	40	5.92
86	6.92	85	6.93
130	7.38	130	7.38
205	7.85	205	7.90
266	8.07	266	8.04
325	8.28	325	...
375	8.32	375	8.30
...	...	1330[1]	8.28

Same proportions; temperature, 0°.

Without Magnet.		With Magnet (10 cells).	
Time.	$Na_2S_2O_3$ required.	Time.	$Na_2S_2O_3$ required.
60	2.70	60.5	2.80
120	3.72	120	3.70
195	4.54	195	4.42
275	4.86	275	4.90
360	5.20	...	...
380	5.70	380	5.80
480	6.06	480	6.10
600	6.43	600	6.60
705	6.71	705	6.75

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Contributions from the Laboratory of Cornell University.

DECOMPOSITION OF SOME DIAZO COMPOUNDS OF NAPHTHALENE WITH ALCOHOL.[2]

BY W. R. ORNDORFF AND F. L. KORTRIGHT.

It has been known for some time that when the salts of diazo compounds of benzene are decomposed with alcohol, two reactions may take place. The diazo group may be replaced by hydrogen, according to the equation

$$C_6H_5.N_2.HSO_4 + C_2H_6O = C_6H_6 + C_2H_4O + N_2 + H_2SO_4;$$

[1] Without magnet.

[2] Prof. Remsen kindly informed the authors of this paper that the work on the decomposition of the diazo compounds of naphthalene would not be taken up in the Johns Hopkins Laboratory.

or the ethoxy group may enter the compound, thus:

$$C_6H_5.N_2.HSO_4 + C_2H_5OH = C_6H_5.OC_2H_5 + N_2 + H_2SO_4.$$

Sometimes both of these reactions take place simultaneously, but generally one or the other prevails.

It is a matter of considerable interest and importance to determine exactly the conditions which give rise to each of these reactions, and though considerable work has been done on this subject, chiefly by Remsen and his pupils, it cannot be said that the problem is as yet by any means solved.

Thinking that the study of the decomposition of the diazo compounds of naphthalene with alcohol might throw some light on this question, the following investigation was undertaken. There are, to be sure, a large number of decompositions of the diazo compounds of naphthalene recorded in the literature, but in few cases is any attention paid to anything save the first reaction, or rather to the products resulting in accordance with the first reaction, and but rarely is any statement made as to the yield obtained. In most cases the reaction has merely served as a means of introducing a hydrogen atom in place of the diazo group, and groups (like the amido and nitro groups), which can readily be converted into the diazo group. Hence the other products formed at the same time were of but little interest, and they have not been isolated or studied. So long as the reaction with alcohol furnished enough material to work with, no attention was paid to the yield.

In the following work the decomposition of some of the simpler diazo-naphthalene compounds with alcohol has been studied, but every product of the reaction has been carefully isolated and examined, and the attempt has been made to obtain, as far as possible, quantitative results. While it is not assumed that these results are more than approximately correct, it is thought that they may be used to give some idea of the course of the reaction.

Preparation of α-Diazo-naphthalene Sulphate.

10 grams of the commercial α-naphthyl amine (melting-point, 45°–47°) were rubbed up with water to a thin paste, 40 grams of concentrated sulphuric acid added, and the whole well ground together in a mortar. Nitrous fumes, obtained in the usual manner from arsenic trioxide and nitric acid, were then passed

into the mixture until they ceased to be absorbed. Care was taken to keep the mixture cool by surrounding it with ice-water and constantly agitating while the nitrogen trioxide was being absorbed. The liquid was then quickly filtered by suction to remove any decomposition products, and the filtrate treated with alcohol and ether, and cooled in a freezing mixture of ice and salt until all the diazo-naphthalene sulphate had crystallised out. The crystals were washed with alcohol and ether and dried on porous paper in the air. From 10 grams of α-naphthyl amine 14 grams of the dry diazo-naphthalene sulphate were obtained, *i. e.* about 79 per cent. of the theoretical yield.

α-diazo-naphthalene sulphate, thus prepared, crystallises in light-yellow, flat needles which retain their yellow color even after being recrystallised from water several times. It is very soluble in water, only slightly so in alcohol, and insoluble in ether. If exposed to the light it rapidly turns green, although it may be preserved for some time if kept in the dark. When heated to 115° it puffs feebly, leaving a black, charred mass, but it does not explode by percussion. An attempt was made to analyse the α-diazo-naphthalene sulphate by the usual method of decomposing the salt with water and collecting and measuring the nitrogen given off. But the results were always too low, probably owing to the formation of an azo dye by the combination of some of the undecomposed diazo salt with the α-naphthol which is formed by the decomposition of α-diazo-naphthalene sulphate with water. It was hence impossible to estimate anything but the acid, and this was done by precipitating with barium chloride and weighing the barium sulphate formed.

I. 0.2505 gram substance gave 23.3 cc. nitrogen at 21° and 732 mm. bar.

II. 0.2325 gram substance gave 21 cc. nitrogen at 19° and 733 mm. bar.

III. 0.2185 gram substance gave 19 cc. nitrogen at 22° and 735 mm. bar.

IV. 0.1455 gram substance gave 13.6 cc. nitrogen at 19° and 738 mm. bar.

V. 0.188 gram substance gave 0.174 gram barium sulphate.

	Calculated for $C_{10}H_7.N_2.HSO_4$.	Found. I.	II.	III.	IV.	V.
N	11.11	9.78	9.70	9.20	10.17	...
SO_3	31.74	...	...	...	...	31.78

Decomposition of α-diazo-naphthalene sulphate in alcohol.—10 grams of the dry α-diazo-naphthalene sulphate and 250 cc. of absolute alcohol were placed in a 500-cc. round-bottomed flask which was connected with a reflux condenser and heated at from 70° to 75° on the water-bath. At about 70° a strong evolution of nitrogen began, and continued without further heating until the diazo salt was completely in solution. The alcohol was colored red, the color becoming deeper and deeper as the reaction proceeded, and the odor of aldehyde was distinctly perceptible throughout the whole experiment. When the evolution of nitrogen had ceased, the contents of the flask were boiled to insure complete decomposition. The excess of alcohol was then distilled off and kept for use in the next decomposition. Here again the odor of aldehyde was distinctly perceptible in the alcoholic distillate.

In this manner 50 grams of the α-diazo-naphthalene sulphate were decomposed. The last alcoholic distillate was diluted with water and a small quantity of naphthalene thus obtained. The total residue from the decomposition of the α-diazo-naphthalene sulphate was then placed in a liter round-bottomed flask and distilled in steam from an acid solution. The residue left in the flask consisted of tarry material and any amido compounds that might be present. The distillate was made alkaline with sodium hydroxide and again distilled in steam. The non-volatile residue left after this distillation was evaporated down to small bulk and acidified with hydrochloric acid; the odor of α-naphthol was noticed, and after a time a few crystals of this substance were deposited, but sufficient to weigh could not be obtained.

By this method of procedure the final distillate was freed from amido and phenol-like bodies. The distillate was now separated by fractioning in steam. A solid passed over first and solidified before leaving the condenser, while the other product followed more slowly as an oil; so that the first receiver contained nothing but the solid, the last an oil, and the intermediate receivers a mixture of the two. By repeating the process with the contents of the intermediate receivers a further separation was made, and after five distillations a complete separation was obtained. The solid was recrystallised from alcohol, and found to form colorless, shining plates, melting at 81°. An analysis gave the following results:

0.228 gram substance gave 0.7860 gram CO_2 and 0.1265 gram H_2O.

	Calculated for $C_{10}H_8$.	Found.
C	93.75 per cent.	93.99 per cent.
H	6.25	6.16

From the physical properties, including the melting-point, and the results of the analysis, there can be no doubt that the substance is naphthalene.

The substance supposed to be ethoxy-naphthalene was dehydrated by dissolving in ether and heating the ethereal solution with calcium chloride. The ether was then distilled off and the oil rectified. Thus prepared, the substance is a light-yellow liquid of a peculiar odor and having a specific gravity of 1.074 at 0° compared with water at 4°. It has the boiling-point 276°, the mercury column being completely in the vapor and the barometric pressure being 745 mm. On exposure to light the oil rapidly turns green. An analysis gave the following results:

0.223 gram substance gave 0.688 gram CO_2 and 0.139 gram H_2O.

	Calculated for $C_{10}H_7.O.C_2H_5$.	Found.
C	83.72 per cent.	84.13 per cent.
H	6.98	6.92

From the results of this analysis and the physical properties, there can be no doubt that the substance is the α-ethoxy-naphthalene first prepared by Schaeffer.[1] As the description given in the literature of the properties of this ether is very meagre, it was thought advisable to prepare it for the purpose of comparison with the product obtained from the decomposition of the α-diazo-naphthalene sulphate with alcohol. The method recommended by Dr. Henriques[2] for the methyl ether of α-naphthol was employed. 30 grams of α-naphthol, 30 grams of absolute alcohol, and 13 grams of concentrated sulphuric acid were mixed in a 500-cc. round-bottomed flask and heated at 140° for 4 hours on a paraffin-bath. The contents of the flask were then poured into water, the lower layer separated, washed with solution of sodium hydroxide, then with water, and finally distilled in steam. The α-ethoxy-naphthalene was then separated from the water by dissolving in ether. The ethereal solution was freed from water by means of calcium chloride. After distilling off the ether, 18 grams of the ethoxy-naphthalene remained. This boiled at 277°, the mercury column being entirely surrounded by vapor

[1] Ann. Chem. (Liebig) **152**, 286. [2] Ibid. **244**, 72.

and the barometric pressure being 748 mm. The liquid had a specific gravity of 1.0746 at 0° compared with water at 4°; turned green by standing in the light; and generally agreed in physical properties with the α-ethoxy-naphthalene obtained from the decomposition of α-diazo-naphthalene sulphate in alcohol. 50 grams of the α-diazo-naphthalene sulphate yielded 10 grams of naphthalene and 8 grams ethoxy-naphthalene. This is equivalent to a conversion of 40 per cent. of the α-diazo-naphthalene sulphate into naphthalene and 23 per cent. into the ethoxy-naphthalene.

Decomposition of α-diazo-naphthalene sulphate in water.—A portion of the α-diazo-naphthalene sulphate was heated with water. At about 80°–90° nitrogen was given off and a quantity of red coloring matter and tar formed. The liquid was filtered while hot, and from the filtrate, on cooling, a quantity of shining plates separated out. These had the melting-point of 96°, and had the odor and general properties of α-naphthol.

Preparation of β-Diazo-naphthalene Sulphate.

The β-naphthyl amine used was the commercial product and melted at 108°–110°. Several methods of preparation of the diazo-naphthalene sulphate were tried before a satisfactory one was found. Unless a considerable excess of sulphuric acid was used, much red material was formed, and the diazo-naphthalene nitrate was apt to crystallise out. The nitric acid either was carried over mechanically from the flask in which the nitrogen trioxide was generated, or was formed by the decomposition of the nitrogen trioxide and tetroxide by water.[1] The diazo nitrate, being much less soluble than the sulphate, crystallised out on standing. Both these difficulties were overcome, however, by adding a large excess of sulphuric acid. The best results were obtained by using four times as much concentrated sulphuric acid by weight as naphthyl amine. From 10 grams of β-naphthyl amine 13 grams of β-diazo-naphthalene sulphate were obtained, which is about 74 per cent. of the theoretical yield. The general details of the method are the same as in the case of the α-diazo-naphthalene sulphate. The diazo salt was washed with alcohol, then with ether, and finally dried before being used. An analysis gave the following results:

I. 0.148 gram gave 14.6 cc. nitrogen at 17° and 754 mm. bar.

[1] Remsen's Advanced Inorganic Chemistry, p. 287.

I. 0.148 gram gave 0.0573 gram H_2SO_4.
II. 0.167 gram gave 16.1 cc. nitrogen at 17° and 754 mm. bar.
II. 0.167 gram gave 0.0652 gram H_2SO_4.

	Calculated for $C_{10}H_7.N_2.HSO_4$.	Found. I.	II.
N	11.11 per cent.	11.21 per cent.	10.98 per cent.
SO_2	31.74	31.63	31.88

Properties of β-diazo-naphthalene sulphate.—The β-diazo-naphthalene sulphate is soluble in water, very slightly soluble in alcohol, and insoluble in ether. It crystallises out from its aqueous solution on the addition of alcohol and ether, and cooling, in flat, needle-shaped yellow crystals. By careful recrystallisation from water these may be obtained nearly colorless, but immediately turn yellow on exposure to the light. The crystals are biaxial, with inclined extinction, and probably belong either to the monoclinic or to the triclinic system. Left exposed to light and air, they rapidly change from yellow to green, and finally to a dark-brown color. This decomposition was shown to be due to the effect of light, and at ordinary temperatures air and moisture have no effect on the salt. On being heated the salt explodes feebly when the temperature reaches 115°. It does not explode by percussion, however.

Decomposition of β-diazo-naphthalene sulphate in alcohol.—30 grams of the β-diazo-naphthalene sulphate were decomposed in 10-gram portions in precisely the same manner as the α-diazo-naphthalene sulphate. The alcohol, after the decomposition, was of a deep-red color, and the odor of aldehyde was faintly perceptible. The residues were united and, after dilution with water, were distilled with steam from a solution made alkaline with sodium hydroxide. The non-volatile residue left in the flask was concentrated by evaporation, filtered to free it from tarry matter, and the filtrate acidified with hydrochloric acid. A precipitate was thus obtained which was filtered off and recrystallised from hot water. The substance then crystallised in colorless shining plates, which melted at 121°, and had the odor and general physical and chemical properties of β-naphthol. The distillate contained now two substances, one of which seemed to be naphthalene, and the other the β-ethoxy-naphthalene. These were separated by fractioning in steam, the method used being essentially the same that was employed in the separation of the naphthalene

from the α-ethoxy-naphthalene, except that here we have to deal with two solids with different melting-points instead of a solid and a liquid. By properly adjusting the temperature of the condenser, however, it was possible to cause one substance (the naphthalene) to solidify before leaving the condenser, and the other (β-ethoxy-naphthalene) to remain liquid until it reached the receiver, and by this means the point of separation could be determined. The substance supposed to be naphthalene crystallised from alcohol in colorless shining plates, melting at 81°. An analysis gave the following results:

0.22 gram gave 0.7545 gram CO_2 and 0.125 gram H_2O.

	Calculated for $C_{10}H_8$.	Found.
C	93.75 per cent.	93.53 per cent.
H	6.25	6.30

The substance is evidently naphthalene.

The other substance, supposed to be the β-ethoxy-naphthalene, crystallised from alcohol in colorless shining plates which gradually turn brown on exposure to the light. When perfectly dry these crystals melted at 37°. They are soluble in alcohol, ether, carbon bisulphide, toluene, petroleum-ether, etc., but insoluble in water. An analysis gave the following results:

0.257 gram gave 0.784 gram CO_2 and 0.159 gram H_2O.

	Calculated for $C_{10}H_7.O.C_2H_5$.	Found.
C	83.72 per cent.	83.19 per cent.
H	6.98	6.87

There can be no doubt from these results that the substance is the β-ethoxy-naphthalene.

Decomposition of β-diazo-naphthalene sulphate by water.—A portion of the β-diazo salt was heated with water. Between 80° and 90° nitrogen was given off in large quantity and at the same time red material and tar were formed. On filtering the hot solution and allowing the filtrate to cool, shining plates crystallised out. These had the melting point (121°), odor and general properties of β-naphthol.

Decomposition of the β-diazo-naphthalene sulphate with hydrochloric acid.—13 grams of the β-diazo-naphthalene sulphate were treated with 200 cc. of 40-per cent. hydrochloric acid, and allowed to stand for several weeks. The flask was then found to be filled with fine crystals. The solution was then treated with an excess

of sodium hydroxide and distilled in steam. A solid distilled with the steam, and this had a pink color which was, however, removed by a second distillation in steam. On recrystallising from alcohol, plate-like crystals with a pearly lustre were obtained, which melted at 59°, and showed all the other properties characteristic of β-chlor-naphthalene. From 13 grams of the diazo salt 4 grams of the β-chlor-naphthalene were obtained, corresponding to a yield of about 50 per cent. of the theoretical quantity. Liebermann[1] prepared β-chlor-naphthalene by boiling the β-diazo-naphthalene sulphate with concentrated hydrochloric acid, but obtained only a small yield of the β-chlor-naphthalene. It would seem, therefore, preferable to allow the decomposition to proceed at ordinary temperatures in this case. A considerable quantity of β-naphthol was formed in this decomposition also.

Preparation of β-Diazo-naphthalene Nitrate.

10 grams of β-naphthyl amine were well rubbed up with water in a mortar, and an equal weight of nitric acid (sp. gr., 1.426) added, care being taken to keep the mixture cool to prevent the formation of nitro compounds. This mixture was then diazotised, and the precipitate of the diazo salt filtered off and recrystallised from water at 40°, by adding alcohol and ether to the aqueous solution and cooling. 10 grams β-naphthyl amine gave 8 grams β-diazo-naphthalene nitrate—about 53 per cent. of the theoretical yield. An analysis of the salt gave the following results:

0.15 gram salt gave 17.8 cc. nitrogen at 20.5° and 747 mm. bar.

0.192 gram salt gave 0.0549 gram HNO_3.

	Calculated for $C_{10}H_7.N_2.NO_3$.	Found.
N	12.90 per cent.	12.99 per cent.
NO_3	28.57	28.21

Properties of β-diazo-naphthalene nitrate.—β-diazo-naphthalene nitrate is soluble in water at ordinary temperatures, but crystallises out when the solution is cooled. It is only slightly soluble in water containing a mineral acid, and is insoluble in absolute alcohol and ether. From water it crystallises in hard, warty crystals. From water to which alcohol and ether have been added, it crystallises in flat yellow needles. It decomposes in the light, turning red; but air and moisture produce little or no effect,

[1] Ann. Chem. (Liebig) **183**, 270.

provided light be excluded. It explodes violently when heated to 100°, and also by percussion.

Decomposition of the β-diazo-naphthalene nitrate in alcohol.—50 grams of the β-diazo-naphthalene nitrate were decomposed, in 10-gram portions, in the same manner as described for the α-diazo-naphthalene sulphate. The odor of aldehyde was quite perceptible during the decomposition. The alcohol was then distilled off, and the residue diluted with water and distilled in steam from an acid solution. From the non-volatile residue in the flask α-nitro-β-naphthol and $\alpha^1\alpha^4$-dinitro-β-naphthol were obtained in small quantity.

The solids, filtered off from the distillate, were separated by fractioning in steam, as before, into naphthalene and β-ethoxy-naphthalene. 50 grams of β-diazo-naphthalene nitrate gave 10 grams of ethoxy-naphthalene and only 2 grams naphthalene. This is equivalent to a conversion of about 26 per cent. of the β-diazo-naphthalene nitrate into β-ethoxy-naphthalene and 7 per cent. into naphthalene. The decomposition of the β-diazo-naphthalene nitrate with water was then shown to be analogous in every respect to the decomposition of the β-diazo-sulphate with water, β-naphthol being formed.

Preparation of β-Ethoxy-naphthalene.

Since the β-ethoxy-napthalene obtained by the decomposition of the diazo compounds with alcohol, had a melting-point of 37° instead of 33°, as given by Schaeffer and others, it was thought advisable to prepare some of the β-ethoxy-naphthalene by another method and compare it with that obtained from the decomposition of the diazo compounds. The method used was that recommended by Schaeffer:[1] 28 grams of the β-naphthol were dissolved in alcohol with 11 grams of potassium hydroxide, and 24 grams of ethyl bromide were added. After boiling this mixture in a flask provided with a reflux condenser, for 3 hours, the potassium bromide was filtered off and the ethoxy-naphthalene distilled in steam. It was then recrystallised from alcohol. It crystallised in shining plates which melted sharply at 37°, even after it had been recrystallised several times from alcohol, and dried in a desiccator over sulphuric acid. Like the ethoxy-naphthalene obtained from the diazo compounds, it gradually turned brown

[1] Ann. Chem. (Liebig) **152**, 287.

in the light; was soluble in alcohol, ether, carbon bisulphide, toluene, petroleum-ether, etc., but insoluble in water. Moreover it resembled the β-ethoxy-naphthalene in general appearance, and had the same odor.

Summary.

The results of this work may be summed up as follows:

The α-diazo-naphthalene sulphate is easily prepared, and when decomposed by alcohol, about 40 *per cent. is converted into naphthalene* and 23 *per cent. into the ethyl ether of α-naphthol.* The β-diazo-naphthalene sulphate and nitrate are rather more difficult to prepare. The sulphate when decomposed with alcohol yields about 30 *per cent. in the form of the ethyl ether of β-naphthol* and 7 *per cent. in the form of naphthalene*, a small quantity of β-naphthol being formed at the same time. The β-diazo nitrate yields results similar to those obtained with the β-diazo-naphthalene sulphate, about 26 *per cent. is converted into the ethyl ether of β-naphthol* and 7 *per cent. into naphthalene.* A small quantity of mononitro- and dinitro-naphthol are also formed at the same time.

The decomposition in water is similar in all cases, the result being a coloring matter, some tar, and a naphthol, α- or β- according as the diazo compound is α- or β-.

When the β-diazo-naphthalene sulphate is decomposed at ordinary temperatures by hydrochloric acid, about 50 per cent. is converted into β-chlor-naphthalene.

From the results obtained by Remsen[1] and his pupils the conclusion was reached that both the position and character of the groups or atoms in the molecule of the diazo compounds exert an influence on the decomposition of these compounds by alcohol. The work just recorded indicates that with diazo-naphthalene compounds, when the diazo group is in the α-position, the tendency is toward the introduction of hydrogen when they are decomposed with alcohol, though both reactions take place simultaneously and the ethyl ether of α-naphthol is formed as well as naphthalene, but in much smaller quantity. When, however, the diazo group is removed to the β-position, the reaction proceeds in exactly the reverse manner; the tendency here is towards the introduction of the ethoxy group in the place of the diazo group, though a small quantity of naphthalene is formed.

[1] This Journal **9**, 387; **11**, 319.

It is proposed to continue this study of the decomposition of the diazo compounds of naphthalene with alcohol, and to investigate the effect upon the reaction of the introduction of different groups in different positions in the molecule. Thus the 1 : 2 α-nitro-naphthyl amine will be converted into the diazo compound and decomposed with alcohol, and the 1 : 2 β-nitro-naphthyl amine will be treated in the same way. The results will be compared, and thus it is hoped the influence of the nitro group may be determined.

CORNELL UNIVERSITY, *October*, 1890.

Contributions from the Chemical Laboratory of Harvard College.

LXXII.—THE REACTIONS OF SODIC ALCOHOLATES WITH TRIBROM-DINITRO-BENZENE AND TRIBROM-TRINITRO-BENZENE.[1]

BY C. LORING JACKSON AND W. H. WARREN.

We were induced to take up this piece of work—although at first sight it might seem to promise little of interest, either in the new compounds formed or in the nature of the reaction—by some experiments in a previous research, which apparently indicated that one of the atoms of bromine in tribrom-dinitro-benzene would be replaced by hydrogen under the influence of sodic ethylate. If this were the case, the work would supply additional material on which to found an explanation of the substitution of bromine by hydrogen in the formation of brom-dinitro-phenyl-malonic ester and allied compounds, described in several previous papers[2] from this Laboratory. Not only has the promise of these experiments been fulfilled, but the work has surpassed in interest all that we expected of it, as it has shown that sodic alcoholates (under which name we class phenolates also) act on tribrom-dinitro-benzene and tribrom-trinitro-benzene in four different ways:

[1] Communicated by the authors, from the Proceedings of the American Academy of Arts and Sciences.

[2] This Journal **11**, 93; **12**, 7, 164, 289, 307 (1889-90).

First. A simple replacement of each atom of bromine by the radicle of the alcoholate. This we have observed only in a single case,—the action of sodic phenolate on tribrom-trinitro-benzene giving trinitro-phloroglucine triphenyl-ether, $C_6(NO_2)_3(OC_6H_5)_3$, melting-point, 175°.

Second. The replacement of two atoms of bromine by two of the radicle of the alcoholate, the third atom of bromine remaining unaltered. Under this head come the actions of sodic ethylate, in the cold, methylate (in part), and phenolate on tribrom-dinitro-benzene, giving $C_6HBr(C_2H_5O)_2(NO_2)_2$, melting-point, 184°; $C_6HBr(CH_3O)_2(NO_2)_2$, melting-point, 237°–238°; and $C_6HBr(C_6H_5O)_2(NO_2)_2$, melting-point, 165°.

Third. The replacement of two atoms of bromine by the radicle of the alcoholate, and the third by hydrogen. Sodic ethylate when hot, and sodic methylate (in part) whether cold or hot, act in this way on tribrom-dinitro-benzene, giving $C_6H_2(C_2H_5O)_2(NO_2)_2$, melting-point, 133°; and $C_6H_2(CH_3O)_2(NO_2)_2$, melting at 167°. These substances can also be made by boiling the corresponding bromine compounds (mentioned under the second class) with the proper alcoholate.

Fourth. The replacement of one, two, or perhaps three of the nitro groups by the radicle of the alcoholate, the three bromine atoms remaining unaffected. This very strange action was observed with sodic ethylate or methylate and tribrom-trinitro-benzene, giving $C_6Br_3C_2H_5O(NO_2)_2$, melting-point, 147°; $C_6Br_3(C_2H_5O)_2(NO_2)$, melting-point, 101°; and $C_6Br_3(CH_3O)_2(NO_2)$, melting-point, 126°.

The product of further action of sodic ethylate, when hot, on tribrom-nitro-resorcin diethyl-ether has not yet been obtained in a state of purity, but we hope to be able to describe it in a later paper.

We have little to say in general about these different modes of action of the alcoholates, except to connect them with previous observations of a similar character, as we think that the number of facts established is still insufficient for the safe foundation of a theoretical explanation of these differences. We hope to continue the work, however, until such a foundation has been secured. The formation of the trinitro-phloroglucine triphenyl-ether (described under the first head) is analogous to the formation of trinitro-phenylene-dimalonic ester from the brom-trinitro-phenyl-

malonic ester,[1] since in the corresponding dinitro compounds the third atom of bromine cannot be replaced by the phenoxy (see second head) or malonic ester radicle, as the case may be, even under more powerful inducements than are needed to bring about this action with the trinitro compounds, thus furnishing another example of the loosening effect of the presence of a third nitro group upon the bromine. The stability of the third atom of bromine in the dinitro compound, so far as replacement by an alcoholate radicle is concerned, mentioned under the second head, is analogous to that of the third bromine atom in dinitro-brom-phenyl-malonic[2] or acetacetic[3] ester in the corresponding dinitro-dibrom compound,[4] and to a less extent in the trinitro derivative;[5] while the replacement of bromine by hydrogen, mentioned under the third head, corresponds closely to the removal of the second atom of bromine from all these substances. In regard to the replacement of the nitro groups instead of the atoms of bromine by ethoxy or methoxy radicles, described under the fourth head, we can only say that the conditions were essentially the same as those under which the bromine in the dinitro compound was replaced, and that as yet we have no hint of an explanation for it, but hope that future experiments will throw some light on the cause of this strange behavior. We may here call attention to the fact, that the replacement of these nitro groups is in direct contradiction to Laubenheimer's rule,[6] that a nitro group is removed only when it is in the *ortho* position to another nitro group, since in the tribrom-trinitro-benzene the three nitro groups are in the *meta* position to each other. Whether this exception to Laubenheimer's rule is due to the fact that it does not apply to sodic ethylate, or to some cause peculiar to the tribrom-trinitro-benzene, must be determined by future experiment.

We also found that neither sodic acetate nor sodic picrate acted on tribrom-dinitro-benzene even at 100°, nor did sodic picrate act on tribrom-trinitro-benzene, which justifies the inference that decidedly acid radicles cannot be taken up by these molecules, which contain so many nitro groups. Also we have repeated the experiment on the action of malonic ester upon tribrom-dinitro-benzene and confirm the negative results previously obtained.[7]

The description of the experimental details of the research occupies the rest of the paper.

[1] This Journal **12**, 20 (1890). [2] Ibid. **11**, 94. [3] Ibid. 167. [4] Ibid. **12**, 296.
[5] Ibid. 9. [6] Ber. d. chem. Ges. **9**, 766 1828. [7] This Journal **12**, 309.

Action of Sodic Ethylate on Tribrom-dinitro-benzene in the Cold.

In order to study this action 20 grams of tribrom-dinitro-benzene (melting-point, 192°: made from symmetrical tribrom-benzene) dissolved in a mixture of 40 cc. of benzene and 90 cc. of absolute alcohol, were treated with an alcoholic solution of the sodic ethylate, made from 3.4 grams of sodium, which gave the proportion of three molecules of sodic ethylate to one of tribrom-dinitro-benzene. That a reaction took place was indicated by the appearance of a pale reddish-yellow color, which gradually increased in intensity to a dark brownish-red, but there was no perceptible evolution of heat. To give the reaction time to run to an end, the mixture was allowed to stand in a corked flask at ordinary temperatures for two or three days, and then was filtered to remove a considerable amount of solid matter which had separated, and the filtrate allowed to evaporate spontaneously. The solid remaining on the filter was washed with water to remove sodic bromide, the presence of which was proved by testing this wash-water with argentic nitrate after acidification with nitric acid, and the portion insoluble in water added to the main product when that had been brought to the same degree of purity. This main product was deposited from the filtrate by the spontaneous evaporation of the solvent, and after washing with water was purified by crystallisation from hot alcohol until it showed the constant melting-point 184°. It is worth mentioning that the earlier crystallisations yielded round woolly masses of fine needles, which were gradually converted, as the substance approached purity, into well formed prisms or plates, since this change in the crystalline habit furnishes a convenient indication of the comparative purity of the substance. The analyses of the substance dried at 100° gave the following results:

I. 0.2616 gram of the substance gave on combustion 0.3426 gram of carbonic dioxide and 0.0904 gram of water.

II. 0.2753 gram of the substance gave 21.9 cc. of nitrogen at a temperature of 25° and a pressure of 745.5 mm.

III. 0.1830 gram of the substance gave, according to the method of Carius, 0.1032 gram of argentic bromide.

	Calculated for $C_6HBr(C_2H_5O_1)_2(NO_2)_2$.	Found. I.	II.	III.
Carbon	35.83	35.72	...	...
Hydrogen	3.28	3.84	...	...
Nitrogen	8.36	...	8.70	...
Bromine	23.89	...	...	24.00

There can be no doubt, therefore, that this substance, melting at 184°, is the brom-dinitro-resorcin diethyl-ether formed by the replacement of two atoms of bromine by two of the ethoxy radicles.

The yield of brom-dinitro-resorcin diethyl-ether is far from good, 20 grams of tribrom-dinitro-benzene giving in no instance more than 4.6 grams of this substance, instead of the 16.5 grams required if the whole of the tribrom-dinitro-benzene had been converted into it, that is, about 28 per cent.; and, in fact, the alcoholic mother-liquors from its purification yielded on evaporation a viscous residue in large quantity, our unsatisfactory work upon which will be described after the statement of the properties of the brom-dinitro-resorcin diethyl-ether. We may give here, however, the result of a determination of the amount of sodic bromide formed in the reaction. 5 grams of tribrom-dinitro-benzene were treated in the cold with the sodic ethylate from 0.9 gram of sodium, in the manner described above, and, after the reaction had come to an end, water was added, the benzene solution removed, and the water extracted three times with benzene, after which it was made up to a volume of 500 cc., and the amount of sodic bromide determined in 20 cc. of this solution; the weight thus obtained calculated on the whole solution gave the result given below as found. The calculated number is the amount of sodic bromide which would be formed if two of the atoms of bromine in the tribrom-dinitro-benzene had been removed.

	Calculated.	Found.
Sodic bromide	1.271 gram	1.194 gram

These results agree as closely as could be expected considering the unavoidable losses in extracting with benzene, and prove that in this case two of the atoms of bromine contained in the tribrom-dinitro-benzene were removed as bromide of sodium.

Properties of Brom-dinitro-resorcin Diethyl-ether,
$C_6HBr(C_2H_5O)_2(NO_2)_2$.

The substance crystallises from alcohol in rather thick, flattened needles of a yellowish-white color, which may attain a length of 1 cm. and sometimes a breadth of 1 mm. The ends are usually square, but less often consist of two planes at a very obtuse angle to each other. The larger crystals seem to be made up of needles united longitudinally, since their ends are apt to be sharply

serrated, or even as much indented as the teeth of a comb. Crystallised from benzene, it formed long slender prisms, sometimes reaching a length of 2 cm., terminated by two planes at an acute angle to each other: these effloresced on exposure to the air. They showed, however, the same melting-point as the crystals obtained from alcohol, and when recrystallised from this solvent gave the plates with square ends described above; they probably contained benzene of crystallisation, which escaped before the temperature had risen to the melting-point of the substance. It melts at 184°; and is not very soluble in alcohol even when hot, less so when cold; slightly soluble in methyl alcohol; nearly insoluble in cold water, very slightly soluble in hot; freely soluble in acetone; soluble in benzene or chloroform; slightly soluble in ether or glacial acetic acid; nearly insoluble in carbonic disulphide, and insoluble in ligroine. Alcohol, or alcohol with a little benzene, is the best solvent for it. Neither sulphuric, nitric, nor hydrochloric acid has any apparent action on it, whether cold or hot.

As has been already stated, the alcoholic mother-liquors from the crystallisation of the brom-dinitro-resorcin diethyl-ether yielded on evaporation a semi-liquid mass of most uninviting properties, in considerable quantity; but although we have given much time to the study of this product, we are unable to make any definite statement in regard to its nature, and have not thought it worth while to postpone the printing of this paper until we could overcome the difficulties in its purification, as it does not lie in the direct line of our research, the principal object of which has been reached by our work on the brom-dinitro-resorcin diethyl-ether and its derivatives. We think it well, however, to give a brief statement of our work on this secondary product, since we have succeeded in isolating a crystalline substance from this viscous mixture by a process of liquation, which we think will prove of value to those chemists who have similar mixtures to deal with. This viscous mass, after standing for some weeks, solidified, but even then was deposited from all its solutions in its original oily condition, and as therefore it could not be crystallised directly we proceeded as follows: Having found that about one quarter of it melted at 50°–60°, we placed it on several layers of filter paper in a dish heated to about 70° by means of a water-bath, and allowed it to stand at this temperature for several days, renewing the filter paper as it was necessary, and towards the end of the process

applying a gentle pressure. The less-fusible residue thus obtained could now be crystallised from alcohol, and yielded a small quantity of a substance melting near 170°, which we took to be impure brom-dinitro-resorcin diethyl-ether, but the amount was so small that we could not recrystallise it often enough to raise the melting-point to the proper temperature, 184°. The principal part of this less-fusible portion melted in the neighborhood of 150°, and proved to be a mixture which, to judge by the melting-point, was the same as an abnormal product occasionally obtained from the process for making brom-dinitro-resorcin diethyl-ether instead of that substance, although we could find no difference in the conditions of the process from those when it gave the normal result. We have not succeeded in separating this mixture into its components, as, after several unsuccessful experiments, the amount remaining at our disposal was too small to continue with any prospect of success the crystallisations, which seemed to purify it very slowly, as they had but little effect on the melting-point. Some analyses of the mixture showed that it contained less carbon and more bromine than brom-dinitro-resorcin diethyl-ether.

The more-fusible portion of the secondary product, which had been absorbed by the papers in the process of liquation, was extracted with alcohol, and the oil thus obtained allowed to stand until it had nearly solidified again, when it was submitted to a second liquation, the more-fusible product of which did not solidify, but only deposited a few crystals. As there were only about 10 grams of this in all, and it manifestly contained two, and, in all probability, three or more substances, we thought there would be little chance of isolating a pure compound from it, and accordingly, after one or two attempts to separate it into its components, its further study was abandoned.

Action of Sodic Ethylate on Tribrom-dinitro-benzene with the Aid of Heat.

As has been shown in the preceding section, sodic ethylate acting on tribrom-dinitro-benzene (melting-point, 192°) in the cold converts it into brom-dinitro-resorcin diethyl-ether melting at 184°; but if, instead, the two substances are heated together, a different product is obtained, which we have found it most convenient to prepare in the following way.—

A solution of 10 grams of tribrom-dinitro-benzene (melting-point,

192°) in 20 cc. of benzene was mixed with the alcoholic solution of sodic ethylate formed from 45 cc. of alcohol and 1.7 gram sodium, giving the proportion of three molecules of the ethylate to one of the tribrom-dinitro-benzene, and the mixture was heated on the steam-bath to gentle boiling for about ten minutes in a flask under a return-condenser. Longer or more violent heating should be avoided, as in this case a decomposition sets in, probably due to the action of the sodic ethylate on the nitro groups, which increases the difficulty in purifying the product. During the boiling the red color of the solution steadily increased in intensity, and a considerable amount of sodic bromide was deposited, together with a brown amorphous substance, which added to the turbidity of the reddish-brown liquid finally obtained. A curious odor was also observed in the solution, which seemed to be characteristic of all the reactions in which bromine was replaced by hydrogen, and was probably due to the secondary product formed from the sodic ethylate, but did not smell like the aldehyde which we had supposed would be this secondary product by the following reaction:

$$C_2H_5ONa + C_6HBr(C_2H_5O)_2(NO_2)_2 = NaBr + C_6H_2(C_2H_5O)_2(NO_2)_2 + C_2H_4O.$$

At the end of the ten minutes the solution was poured into an evaporating dish and allowed to evaporate to dryness spontaneously, washed with water to remove sodic bromide, and the reddish-brown substance insoluble in water, purified by crystallisation from alcohol with the aid of boneblack until it showed the constant melting-point 133°, when it was dried at 100°, and analysed with the results given under I and III. More than a year ago G. D. Moore, with one of us, obtained under somewhat different conditions the same substance, as shown by the melting-point and crystalline form, and we therefore add the analyses made of it by Dr. Moore at that time, II, IV and V.

I. 0.2200 gram of the substance gave on combustion 0.3752 gram of carbonic dioxide and 0.0950 gram of water.

II. 0.2320 gram of the substance gave 0.3990 gram of carbonic dioxide and 0.0995 gram of water.

III. 0.2112 gram of the substance gave 21 cc. of nitrogen at a temperature of 26° and a pressure of 754.8 mm.

IV. 0.2299 gram of the substance gave 22.3 cc. of nitrogen at a temperature of 23° and a pressure of 762.2 mm.

V. 0.2142 gram of the substance gave 20.3 cc. of nitrogen at a temperature of 22.5° and a pressure of 767 mm.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$.	Found. I.	II.	III.	IV.	V.
Carbon	46.88	46.50	46.90	...	...	...
Hydrogen	4.69	4.80	4.77	...	...	...
Nitrogen	10.94	...	...	10.96	10.96	10.81

It contained no bromine.

These analyses prove that the substance is the dinitro-resorcin diethyl-ether, which must have been formed from the tribrom-dinitro-benzene $C_6HBr_3(NO_2)_2$ by the replacement of two of its atoms of bromine by two ethoxy radicles (C_2H_5O), the third by hydrogen, and we have here another case of the curious replacement of bromine by hydrogen in preference to its replacement by a radicle combined with sodium, which was first observed in the study of the action of sodium malonic ester upon tribrom-dinitro-benzene, and which induced us to undertake the present investigation. Since this dinitro-resorcin diethyl-ether melts at 133°, it is isomeric with the one[1] already known, melting at 75°.

Properties of Dinitro-resorcin Diethyl-ether, $C_6H_2(C_2H_5O)_2(NO_2)_2$.—This substance crystallises by cooling from an alcoholic solution in long, slender needles or flattened prisms with a sharp point. If the alcoholic solution is allowed to evaporate spontaneously, it forms some curling hair-like crystals which are very characteristic. The crystals from alcohol are also apt to form clumps of radiating hairs shaped somewhat like a toadstool, especially if the substance is not absolutely pure. From ether it crystallises in needles combined longitudinally into prisms with prickly ends; from chloroform, in radiating needles. It melts at 133°, and is nearly insoluble in water, although apparently a little more soluble in it hot than cold; not very soluble in cold alcohol, freely in hot; more soluble in methyl than in ethyl alcohol, whether cold or hot; freely soluble in chloroform, glacial acetic acid, or acetone; soluble in benzene; slightly soluble in ether; very slightly in carbonic disulphide; essentially insoluble in ligroine. Alcohol is the best solvent for it. Strong sulphuric acid dissolves it in the cold, forming a yellow solution; strong nitric acid has no action on it when cold, but gives a colorless solution if heated with it; strong hydrochloric acid has no action on it, whether hot or cold.

[1] Aronheim: Ber. d. chem. Ges. 12, 32.

Conversion of Brom-dinitro-resorcin Diethyl-ether into Dinitro-resorcin Diethyl-ether.

It has been shown in the two preceding sections that the action of sodic ethylate on tribrom-dinitro-benzene differs according to the conditions under which it takes place, since in the cold brom-dinitro-resorcin diethyl-ether is formed, but when the mixture is heated the third atom of bromine is also removed and replaced by hydrogen, so that the product is the dinitro-resorcin diethyl-ether. In order to throw more light on this substitution of hydrogen for the third atom of bromine we next tried the action of sodic ethylate, when heated, on the brom-dinitro-resorcin diethyl-ether, as it was possible that this substitution could take place only at the moment of the replacement of the other two atoms of bromine by the ethoxy radicles, and in that case boiling sodic ethylate would not convert the ready-formed brom-dinitro-resorcin diethyl-ether into the dinitro-resorcin diethyl-ether. Accordingly 3 grams of brom-dinitro-resorcin diethyl-ether were mixed with the sodic ethylate from 0.6 gram sodium dissolved in alcohol,[1] and the mixture heated to gentle boiling for about ten minutes in a flask under a return-condenser, when it had taken on a dark-red color, and the curious odor observed in making the dinitro-resorcin diethyl-ether was very perceptible. The solvent was then allowed to evaporate spontaneously, and the residue washed with water, which removed sodic bromide (as was proved by the addition of argentic nitrate) and a red impurity. It was then purified by crystallisation from hot alcohol, until it showed a constant melting-point, when we found that this treatment had lowered the melting-point from 184°, that of the brom-dinitro-resorcin diethyl-ether, to 133°, that of the dinitro-resorcin diethyl-ether, which substance the product also resembled in appearance and solubility. To remove all doubt about its nature it was dried at 100° and analysed, with the following results:

0.1378 gram of the substance gave on combustion 0.2354 gram of carbonic dioxide and 0.0616 gram of water.

	Calculated for $C_6H_2(C_2H_5O)_2(NO_2)_2$.	Found.
Carbon	46.88	46.58
Hydrogen	4.69	4.97

[1] We found that benzene must not be added in this case, as it seemed to interfere with the progress of the reaction.

This proves that the substance is the dinitro-resorcin diethyl-ether, and that the principal action of the hot sodic ethylate upon the brom-dinitro-resorcin diethyl-ether was the replacement of its bromine by hydrogen.

After the experiment just described had proved that the bromine in brom-dinitro-resorcin diethyl-ether could be replaced by hydrogen by means of boiling sodic ethylate, it seemed of interest to determine whether the same change could be brought about by other reagents, and we tried, first, alcohol alone, which might produce this action by giving aldehyde and hydrobromic acid as secondary products, although this was not at all probable, since the brom-dinitro-resorcin diethyl-ether was purified by crystallisation from hot alcohol; and indeed, after boiling it with alcohol for a long time in a flask under a return-condenser, the result was entirely negative, nothing but unaltered brom-dinitro-resorcin diethyl-ether, melting at 184°, being obtained on evaporation of the alcoholic solution.

From the action of malonic ester on brom-dinitro-resorcin diethyl-ether we expected better results, because, although it is true that malonic ester has no action on tribrom-dinitro-benzene,[1] in the formation of brom-dinitro-phenyl-malonic ester it seems to replace one atom of bromine by hydrogen in the dibrom-dinitro-phenyl-malonic ester[2] (which we must infer is an intermediate product in the reaction), and if this replacement is made possible by the presence of the malonic ester radicle $CH(COOC_2H_5)_2$ in the molecule, we thought that perhaps the two ethoxy radicles in brom-dinitro-resorcin diethyl-ether might produce the same effect. The result of the experiment, however, was again negative, whether carried on cold or hot, as the solid product melted at 184°; and the same result was obtained if acetacetic ester was used instead of malonic ester, although in this latter case the substances were boiled together for four hours.

Supposing from the negative results of these experiments that the presence of sodium malonic ester as well as malonic ester was necessary for the replacement of bromine by hydrogen in the hypothetical dibrom-dinitro-phenyl-malonic ester (leading to an immediate formation of acetylene-tetracarbonic ester[3] as the secondary product), we tried the action of such a mixture, that is,

[1] See This Journal **12**, 309, and the concluding section of this paper.
[2] This Journal **11**, 547. [3] Ibid. **12**, 16.

one molecule of malonic ester to one molecule of sodium malonic ester, upon the brom-dinitro-resorcin diethyl-ether in alcoholic solution, at first in the cold for five days, that is, under the conditions used in the preparation of brom-dinitro-phenyl-malonic ester, but at the end of this time no sodic bromide could be detected, and essentially all the original ether was recovered unaltered. In another experiment the mixture was heated on the steam-bath for fifteen minutes, but, although a distinct red color appeared, the reaction could have been at best a very limited one, as essentially all the brom-dinitro-resorcin diethyl-ether was recovered unaltered, so that the new substance, if any were formed, was present in such small quantity that we were unable to detect it. It follows from these experiments, that the atom of bromine in brom-dinitro-resorcin diethyl-ether is more firmly attached to the molecule than the second atom of bromine in the hypothetical dibrom-dinitro-phenyl-malonic ester, since this is replaced by hydrogen through the agency of malonic and sodium malonic esters, or more probably by the malonic ester alone, considering the formation of tartronic acid.[1]

Action of Sodic Methylate on Tribrom-dinitro-benzene.

We took up this subject because it was possible that the action of sodic methylate might be different from that of sodic ethylate described in the preceding sections; but we have found that this is not the case, unfortunately at an expense of time and labor entirely out of proportion to the value of the results obtained.

Our experience with sodic ethylate induced us at first to try the action of sodic methylate in the cold; but as we soon found that the same products were obtained when the action was assisted by heat, we have usually proceeded in this way, since, when boiling, the reaction runs to an end in ten minutes, whereas in the cold it takes about two days. Finally we adopted the following method: 10 grams of tribrom-dinitro-benzene dissolved in about 20 cc. of benzene were mixed with a solution in methyl alcohol of the sodic methylate from 1.7 gram of sodium, and the mixture boiled for ten minutes on the steam-bath in a flask fitted with a return-condenser, when a clear red solution was obtained, which on cooling deposited white crystals. These were filtered out, the filtrate allowed to evaporate to dryness, and the residue and

[1] This Journal **11**, 546.

crystals extracted three or four times with small amounts of hot alcohol, as in this way a viscous impurity was removed, the nature of which will be considered later. The purification of the less-soluble portion offered great difficulties, which was the more surprising because it was but slightly soluble in any solvent, so that the separation of it from the viscous product was very easy, and by crystallisation from hot alcohol we soon obtained a substance showing the constant melting-point 237°–238°; but the results of its analysis did not agree with those calculated for brom-dinitro-resorcin dimethyl-ether, as is shown by the following comparison:

	Calculated for $C_6HBr(NO_2)_2(OCH_3)_2$.	Found.
Carbon	31.27	32.78
Hydrogen	2.28	3.21
Nitrogen	9.12	10.64
Bromine	26.05	25.02

As these analyses seemed to indicate that the substance was not pure, we crystallised it again several times, using glacial acetic acid as the solvent; and after a new set of analyses had yielded no better results than those given above, we recrystallised six or seven times, this time from acetone, but with no better agreement of the percentages derived from analysis with those corresponding to the formula. As the substance crystallised very well, we were inclined to think at first that we had a compound different from the brom-dinitro-resorcin dimethyl-ether, probably with a higher molecular weight. Accordingly, we tried to determine the molecular weight of the substance by the method of Raoult, and obtained numbers not too far removed from the molecular weight of brom-dinitro-resorcin dimethyl-ether; but we do not think these results of any value, as the solubility of the substance in glacial acetic acid was so slight that the differences in the depression of the freezing-point for different molecular weights fell almost within the limits of error of the process. After many other experiments to determine the nature of this substance, which led to no result, we found at last in the anilido compound derived from it a body which could be purified by crystallisation, and from the analysis of which a safe inference could be drawn in regard to the nature of the substance melting at 237°–238°.

Anilido-dinitro-resorcin Dimethyl-ether,
$C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.

This substance was prepared by heating the body melting at 237°–238°, with an excess of aniline at a temperature somewhat above 100° for about twelve hours, when the product was acidified with dilute sulphuric acid, washed carefully with water till all aniline salts were removed, and purified by crystallisation from hot alcohol until it showed the constant melting-point 196°. During this crystallisation we observed indications that we were dealing with a mixture, as the constant melting-point 196° was reached only when working with large quantities and after repeated crystallisation; but the impurity, which seemed to melt near 206°, was present in such small quantity that we were unable to determine its nature. The pure anilido compound was dried at 100°, and analysed with the following results:

I. 0.2973 gram of the substance gave on combustion 0.5733 gram of carbonic dioxide and 0.1167 gram of water.

II. 0.2064 gram of the substance gave 23.7 cc. of nitrogen at a temperature of 22.5° and a pressure of 761 mm.

	Calculated for $C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.	Found. I.	II.
Carbon	52.66	52.59	...
Hydrogen	4.08	4.36	...
Nitrogen	13.16	...	13.02

From this it appears that the anilido compound is anilido-dinitro-resorcin dimethyl-ether, and consequently that the substance melting at 237°–238° must be essentially the brom-dinitro-resorcin dimethyl-ether, but that it contains some impurity which cannot be removed from it even by very long-continued crystallisation from alcohol, glacial acetic acid, or acetone; and this view is confirmed by the behavior of the anilido compound on crystallisation described above. Another determination of the nature of the substance melting at 237°–238° will be given below when we describe its conversion into dinitro-resorcin dimethyl-ether. The fact that in the action described above only the bromine was replaced by the aniline radicle C_6H_5NH, surprised us, as we had expected that the methoxy groups would undergo a similar replacement, owing to their position in regard to the nitro groups.

Properties of Anilido-dinitro-resorcin Dimethyl-ether, $C_6H(C_6H_5NH)(CH_3O)_2(NO_2)_2$.

This substance forms bright-yellow needles, or very slender prisms, which show some tendency to unite in radiating groups. It melts at 196°, and is nearly but not quite insoluble in water; not very soluble in cold ethyl or methyl alcohol, more soluble in hot; freely soluble in chloroform or acetone; soluble in benzene or glacial acetic acid; slightly in ether; very slightly in carbonic disulphide, and insoluble in ligroine. Alcohol is the best solvent for it.

Properties of Brom-dinitro-resorcin Dimethyl-ether, $C_6HBr(CH_3O)_2(NO_2)_2$.

Although we did not succeed in getting this substance absolutely pure, we think it worth while to give its properties, as the slight amount of impurity present could have influenced them but little, and they differ rather strikingly from those of the corresponding ethyl compound. When crystallised from glacial acetic acid by cooling, it forms prisms terminated by a single rhombic plane at an acute angle to the sides of the prism, which are so short that the crystal looks almost like a rhombohedron; these crystals are white with a faint yellowish tinge, and often a millimeter long. When crystallised by slow evaporation of the glacial acetic acid solution, the crystals are converted into long, well-formed prisms, and the single rhombic plane which forms the principal termination is usually modified by other smaller planes. The highest melting-point which we have obtained for this substance was 237°–238°, but the analyses showed that even when melting at this point it was still far from pure. It is nearly insoluble in water, its solubility being perhaps somewhat increased by boiling; very slightly soluble in ethyl or methyl alcohol, the solubility somewhat increased by heat; slightly soluble in acetone, benzene, chloroform, glacial acetic acid, or nitrobenzene; very slightly in ether or carbonic disulphide; insoluble in ligroine. The best solvent for it is acetone or glacial acetic acid, as it is more soluble in these liquids than in any other; but its slight solubility in all the common solvents is one of its most striking properties.

Dinitro-resorcin Dimethyl-ether, $C_6H_2(CH_3O)_2(NO_2)_2$.

This substance was formed in addition to the brom-dinitro-resorcin dimethyl-ether by the action of sodic methylate in methyl alcoholic solution upon tribrom-dinitro-benzene, whether the substances were heated together, or the action was allowed to take place in the cold. The action of sodic methylate, therefore, on account of this indifference to the effect of temperature, is unlike that of sodic ethylate, which gave only brom-dinitro-resorcin diethyl-ether in the cold, and, when heated, only dinitro-resorcin diethyl-ether. The dinitro-resorcin dimethyl-ether, which was formed in comparatively small quantity, was obtained from the alcoholic washings and mother-liquors of the substance melting at 237°–238°. The residue left after the evaporation of the alcohol was a viscous mass, which contained, in addition to the substance of which we were in search, an oily impurity similar to that obtained from the ethyl compound, and a little brom-dinitro-resorcin dimethyl-ether. It was therefore a matter of some difficulty to isolate a pure substance from it, but we finally succeeded by repeated crystallisation from hot alcohol, during which crystals of two sorts were obtained, one consisting of white needles turning brown in the air, the other of lemon-yellow rhombic crystals, which appeared especially during the earlier parts of the crystallisation, and were gradually converted into the white needles. That the difference between the two forms consisted in the presence of one molecule of alcohol of crystallisation in the white needles was shown by the following analytical results:

I. 0.9817 gram of the air-dried substance lost 0.0177 gram at 100°.

II. 0.7617 gram of the substance dried *in vacuo* lost 0.0142 gram at 100°.

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2C_2H_6OH$.	Found. I.	II.
Alcohol	16.79	18.03	18.64

These numbers agree somewhat better with the percentages calculated for three molecules of water of crystallisation; but, apart from the improbability that the substance would take up water when crystallised from ordinary alcohol, we have found that the liquid given off, when the needles were heated in a test tube, dissolved the crystals clinging to the side of the tube, and that the substance dried at 100°, when recrystallised from absolute

alcohol, gave white prisms like those whose analysis is given above. The analysis which follows was made with the white needles after they had been dried at 100°, and therefore freed from their alcohol of crystallisation.

0.2688 gram of the substance gave on combustion 0.4092 gram of carbonic dioxide and 0.1027 gram of water.

	Calculated for $C_6H_2(CH_3O)_2(NO_2)_2$.	Found.
Carbon	42.11	41.52
Hydrogen	3.51	4.25

The substance contains no bromine.

From these results it is evident that the substance is the dinitro-resorcin dimethyl-ether, but its melting-point, 167°, shows that it is isomeric with the substance[1] of this composition already known, which melts at 67°.

Properties.—The dinitro-resorcin dimethyl-ether was obtained crystallised with one molecule of alcohol, and also in crystals free from alcohol. When containing a molecule of alcohol it forms sheaves or bunches of white needles, or slender prisms often a centimeter long terminated by two planes at a very obtuse angle to each other, or, less often, a single plane at an acute angle to the sides; frequently also a single plane at right angles to the sides was observed, but we were inclined to consider this due to cleavage rather that a real termination of the crystal. These two prevailing forms, the two planes at an obtuse angle and the single plane at a right angle, give a general square-ended effect to the crystals which is characteristic. On exposure to the air these crystals turn purplish-brown. When containing no alcohol of crystallisation, it forms short, thick and broad crystals, apparently prisms of the monoclinic system, somewhat like certain felspars, or rhombic crystals made up by the twinning of such prisms along one diagonal of the rhomb, and having a lemon-yellow color, which is not altered by exposure to the air. The melting-point is 167°, but the white needles melt a degree and a half below this point, probably on account of the presence of the vapor of alcohol. The substance is nearly insoluble in cold water, somewhat more soluble in hot; slightly soluble in cold ethyl or methyl alcohol, more soluble in hot; very freely soluble in acetone; freely in glacial acetic acid or benzene; soluble in chloroform; slightly

[1] Hönig: Ber. d. chem. Ges. **11**, 1041.

soluble in ether, less so in carbonic disulphide; and essentially insoluble in ligroine. The best solvent for it is boiling alcohol. The white needles, if recrystallised from chloroform or glacial acetic acid, give crystals of the lemon-yellow variety (that is, free from alcohol). Strong sulphuric acid in the cold has little, if any, action on it, when hot it dissolves a small quantity, forming a yellow solution; strong nitric acid does not dissolve it in the cold, but when hot dissolves it, forming a very pale-yellowish solution; strong hydrochloric acid has no action on it, either cold or hot.

The dinitro-resorcin dimethyl-ether was also made from the substance melting at 237°–238° (impure brom-dinitro-resorcin dimethyl-ether) by heating it to boiling with sodic methylate in methyl-alcohol solution for one hour in a flask with a return-condenser, at the end of which time the formation of dinitro-resorcin dimethyl-ether was proved by the melting-point, 167°, and the characteristic form of the crystals. This experiment shows that the action with the methyl compounds is similar to that with the ethyl compounds already described, but it takes place less easily, since in the ethyl series heating for ten minutes was sufficient to complete the action, whereas with the methylate boiling for an hour was necessary. This formation of dinitro-resorcin dimethyl-ether furnishes us with another and most convincing proof that the substance melting at 237°–238° is essentially brom-dinitro-resorcin dimethyl-ether, confirming our work with the anilido compound.

Some experiments on the action of sodic iso-amylate upon tribrom-dinitro-benzene gave under the conditions used with the ethylate and methylate only a viscous liquid, which did not solidify even after standing for two months, and as it did not distil with steam we decided that its purification would take more time than our interest in this subject would warrant, and accordingly abandoned this branch of the research.

Action of Sodic Phenolate on Tribrom-dinitro-benzene.

To study this action, 30 grams of tribrom-dinitro-benzene, dissolved in a mixture of alcohol and benzene, were mixed with an alcoholic solution of 20.8 grams of phenol previously converted into the sodium salt by the addition of a concentrated aqueous solution of 8.8 grams of sodic hydrate, and allowed to stand at ordinary temperatures over night. The amount of phenol used corres-

ponds to three molecules for every molecule of the tribrom-dinitro-benzene. The solution turned light-yellow, and deposited some crystals, apparently tribrom-dinitro-benzene, but the action was very limited, if any had taken place. Accordingly the mixture was heated on the steam-bath in a flask with a return-condenser for ten to twelve hours, when it turned dark-brown, and after the solvent had been distilled off there was left in the flask a brownish, viscous residue of the most uninviting appearance. This was thoroughly washed with water, and then allowed to stand for several days, which rendered it more solid; it was then washed three or four times with small quantities of cold alcohol, which removed much, but not by any means all, of the oily impurity, and the still-viscous residue recrystallised from a mixture of alcohol and benzene until it showed the constant melting-point 165°, when it was dried at 100°, and analysed with the following results:

I. 0.3128 gram of the substance gave on combustion 0.5781 gram of carbonic dioxide and 0.0790 gram of water.

II. 0.2051 gram of the substance gave according to the method of Carius 0.0888 gram of argentic bromide.

	Calculated for $C_6HBr(C_6H_4O)_2(NO_2)_2$.	Found. I.	II.
Carbon	50.12	50.40	...
Hydrogen	2.55	2.81	...
Bromine	18.57	...	18.43

These results prove that the substance is the brom-dinitro-resorcin diphenyl-ether. We may add, that in one preparation, in addition to this a substance was obtained, crystallising in square plates and melting at about 158°, but in too small quantity for analysis, and we have not succeeded in making it again. We can say nothing about the nature of the oily product of the reaction, as we could find no way of purifying it.

Properties of Brom-dinitro-resorcin Diphenyl-ether, $C_6HBr(C_6H_5O)_2(NO_2)_2$.

This substance forms woolly masses of irregularly-radiating needles which under the microscope appear long and rather slender, with either a rounded sharpening at the point or else very sharp, tapering ends; the substance is white at first, but turns to a pale chocolate-brown on exposure to the air. It melts at 165°,

and is very slightly soluble in water whether cold or hot; slightly soluble in cold alcohol, more soluble in hot, but not freely; rather more soluble in methyl than in ethyl alcohol, but not freely soluble even in this when hot; very freely soluble in chloroform; freely in benzene or acetone; soluble in ether; slightly soluble in glacial acetic acid or carbonic disulphide; very slightly soluble in ligroine. The best solvent for it is a mixture of alcohol and benzene. Neither strong sulphuric nor hydrochloric acid seemed to have any action on it, hot or cold; but strong nitric acid dissolved it after a few minutes' heating, and gave on dilution a new substance melting above 200°, probably a nitro compound. Sodic hydrate in solution has no perceptible action on the substance.

The removal of the bromine from the brom-dinitro-resorcin diphenyl-ether interested us especially, as the somewhat more acid nature of the phenol radicle (C_6H_5O) would, we thought, exercise a marked influence on it; unfortunately, however, the product has proved completely unmanageable, so that we can give only a very imperfect account of this action. We tried first hot sodic ethylate, but found that the substance was much more susceptible to its action than the corresponding ethyl or methyl compounds, showing signs of decomposition by turning dark when the mixture was heated for ten minutes; and although a less-colored solution was obtained when we heated for only three or four minutes on the steam-bath, the residue left after spontaneous evaporation of the alcohol was a dark-colored, oily liquid which showed no signs of solidification, but gradually changed into a black tar after standing some months, and could not be brought into a state fit for analysis by any method we have been able to devise. The aqueous wash-water from this substance contained sodic bromide, so that there is no question that the bromine had been removed, but we are unable to determine whether it has been replaced by hydrogen or ethoxyl.

We thought it possible that the bromine might be removed from brom-dinitro-resorcin diphenyl-ether by phenol, tribrom-phenol being formed; but after heating the substances together on the steam-bath for two days, essentially all the brom-dinitro-resorcin diphenyl-ether was recovered unaltered. A mixture of sodium malonic ester with an excess of malonic ester seemed to have more effect, as the liquid turned first pale yellow and then red. It was allowed to stand in the cold for several weeks, when it was found that a

small amount of sodic bromide had been formed; but the action was a very limited one, as almost all of the brom-dinitro-resorcin diphenyl-ether was recovered unaltered, and the new compound was present in such small quantity that we did not succeed in isolating it.

Experiments with Tribrom-trinitro-benzene.

After we had found that the bromine in brom-dinitro-resorcin diethyl-ether could be replaced with hydrogen by the action of hot sodic ethylate, it became interesting to find out whether this was the same atom of bromine which undergoes a similar replacement in making brom-dinitro-phenyl-malonic ester, that is, the atom which stands between the two nitro groups, and the easiest way to do this seemed to be to take up the study of the tribrom-trinitro-benzene, in which all the atoms of bromine are similarly placed. This we have done, but without the desired result, as the sodic alcoholates show with tribrom-trinitro-benzene actions entirely different from those with the corresponding dinitro compound.

Action of Sodic Ethlyate on Tribrom-trinitro-benzene.

To study this action 10 grams of tribrom-trinitro-benzene (symmetrical, melting at 285°) were covered with ordinary alcohol in a flask, and to the mixture of crystals and alcohol 1.6 gram of sodium (three atoms of sodium would be a little over 1.5 gram) previously converted into sodic ethylate was added, in small portions at a time, the flask being immersed in cold water and shaken after each addition so as to avoid a rise of temperature[1] in any part of the liquid. The first drop of the alcoholic solution of sodic ethylate turned red on touching the liquid in the flask, and then faded to yellow; but as the remainder of the sodic ethylate was added, the color increased in intensity, until at last it had become a deep blood-red, while at the same time the undissolved solid began to diminish in quantity, and finally entirely disappeared, leaving a clear solution, thus showing that all the tribrom-trinitro-benzene had been used up, as it is nearly insoluble in alcohol. The mixture was allowed to stand over night, when it was found that a fresh amount of solid had been deposited: the solvent was then allowed to evaporate spontaneously, the residue (including the

[1] If the tribrom-trinitro-benzene was dissolved in benzene, the action was so violent that it was almost impossible to avoid a rise of temperature.

solid which had separated over night) washed with water until free from inorganic matter, and purified by crystallisation from alcohol until it showed the constant melting point 101°, after which it was dried at about 70° and analysed, with the following unexpected results:

I. 0.3519 gram of the substance gave on combustion 0.3427 gram of carbonic dioxide and 0.0742 gram of water.

II. 0.2883 gram of the substance gave on combustion 0.2795 gram of carbonic dioxide and 0.0632 gram of water.

III. 0.3165 gram of the substance gave 9.8 cc. of nitrogen at a temperature of 25° and a pressure of 764.7 mm.

IV. 0.2315 gram of the substance gave by the method of Carius 0.2912 gram of argentic bromide.

V. 0.1588 gram of the substance gave 0.2002 gram of argentic bromide.

	Calculated for $C_6Br_2NO_2(C_2H_5O)_2$.	Found. I.	II.	III.	IV.	V.
Carbon	26.79	26.56	26.43	...	...	...
Hydrogen	2.23	2.34	2.44	...	...	...
Nitrogen	3.13	...	...	3.48	...	...
Bromine	53.57	...	...	...	53.55	53.64

These results show that the action is entirely different from that with tribrom-dinitro-benzene, for this gave with sodic ethylate brom-dinitro-resorcin diethyl-ether, $C_6HBr(OC_2H_5)_2(NO_2)_2$, by the replacement of two atoms of bromine by two ethoxy radicles; whereas here, under the same conditions, we have the tribrom-nitro-resorcin diethyl-ether, which must have been formed by the replacement of two nitro groups by two ethoxy radicles. We have sought the confirmation of our analytical results, which their strangeness certainly requires, in the examination of the sodium salt formed in the reaction, which should be sodic nitrite instead of the sodic bromide which would have been formed if the reaction had run as it did with the dinitro compound. The aqueous washings from a new preparation of the substance melting at 101°, gave after acidification with nitric acid only a faint turbidity with argentic nitrate, showing that only a trace of sodic bromide had been formed, whereas from other portions of the wash-water we obtained the strongest reactions for a nitrite, as the following statement shows: Potassic iodide and starch-paste acidified with dilute sulphuric acid gave a very deep blue color; ferrous sul-

phate and sulphuric acid, a brownish-black color throughout the whole solution; a portion of the residue from evaporation of the wash-water added to strong sulphuric acid and phenol gave a reddish-brown color quickly passing through green to blue; strong sulphuric acid added to the residue from the evaporation of the wash-water gave off a gas recognised as nitrous fumes by the red color, and odor. There can be no doubt, therefore, that the sodic ethylate acts on tribrom-trinitro-benzene according to the following reaction:

$$C_6Br_3(NO_2)_3 + 2C_2H_5ONa = C_6Br_3NO_2(C_2H_5O)_2 + 2NaNO_2.$$

We may add that, as we felt we could not be too careful in a case of this kind, the second specimen of tribrom-nitro-resorcin diethyl-ether was made from a quantity of tribrom-trinitro-benzene, the purity of which had been proved by analysis as well as by the melting-point—found: 53.60 per cent. of bromine instead of the 53.33 per cent. required by the formula.

As potassium compounds behave in many respects differently from the corresponding sodium compounds, we have repeated the experiment with potassic in place of sodic ethylate, but with the same result, that is, tribrom-nitro-resorcin diethyl-ether, melting at 101°, and potassic nitrite.

Properties of Tribrom-nitro-resorcin Diethyl-ether, $C_6Br_3NO_2(OC_2H_5)_2$.—This substance forms well-developed, white, flat prisms, usually with square ends, but sometimes terminated by two planes at an obtuse angle. It melts at 101°, and is very slightly if at all soluble in water, whether cold or hot; easily soluble in cold ethyl or methyl alcohol, still more freely in hot; very freely soluble in chloroform; freely in benzene; soluble in ether, acetone, carbonic disulphide, or glacial acetic acid; slightly soluble in ligroine. Hot alcohol is the best solvent for it. The three strong acids seem to have no action on it, whether they be hot or cold. Aniline dissolves it, but has no other action on it at ordinary temperatures, or even at 150°; at higher temperatures a substance similar to rosaniline is formed. A mixture of malonic ester and sodium malonic ester was allowed to stand for several weeks with an alcoholic solution of this substance; but, although at the end of this time the liquid had assumed a slight reddish color, and a little sodic bromide (but no nitrite) had been formed, the action was so limited that the only organic compound which could be detected in the product was unaltered tribrom-nitro-resorcin

diethyl-ether, melting at 101°. It appears from these experiments that the tribrom-nitro-resorcin diethyl-ether is not an especially reactive substance, and yet when it was boiled with an alcoholic solution of sodic ethylate a reaction took place, as was shown by the dark color which the solution assumed, and the formation of a considerable amount of sodic nitrite, proved by the test with potassic iodide, starch, and dilute sulphuric acid. Unfortunately the end of the term prevented us from isolating the organic product, or, more probably, products, of this reaction, but the work will be continued next year.

Tribrom-dinitro-phenetol, $C_6Br_3(NO_2)_2OC_2H_5$.

In our first experiment on the action of sodic ethylate on tribrom-trinitro benzene the conditions were somewhat different from those described above, which gave us the tribrom-nitro-resorcin diethyl-ether, since benzene was used in addition to alcohol as a solvent, and no pains were taken to cool the liquid, although the reaction produced a noticeable amount of heat. The product, which was worked up by spontaneous evaporation of the solvent, washing, and recrystallisation from alcohol, showed the constant melting-point 147°, instead of 101°. Upon trying to make more of this substance in the same way, we obtained a product which was evidently a mixture of the substance melting at 101° and that melting at 147°, but the end of the term has prevented us from making out the exact conditions necessary for the production of the substance melting at 147° as the principal product. Fortunately the amount of this substance made in our first experiment was sufficient for its characterisation. It was dried at 100°, and analysed with the following results:

I. 0.1607 gram of the substance gave on combustion 0.1237 gram of carbonic dioxide and 0.0263 gram of water.

II. 0.2142 gram of the substance gave by the method of Carius 0.2683 gram of argentic bromide.

III. 0.1736 gram of the substance gave 0.2192 gram argentic bromide.

	Calculated for $C_6Br_3(NO_2)_2OC_2H_5$.	Found. I.	II.	III.
Carbon	21.38	20.99	...	...
Hydrogen	1.11	1.82	...	...
Bromine	53.46	...	53.31	53.74

Properties.—The tribrom-dinitro-phenetol occurs in white, well formed, slender, nearly-square prisms, often a centimeter long,

terminated by a single plane at an acute angle to the sides. It melts at 147°, and is soluble in cold ethyl or methyl alcohol, more freely in hot; freely soluble in benzene, chloroform, glacial acetic acid, or acetone; soluble in ether or carbonic disulphide; almost insoluble in ligroine. The best solvent for it is hot alcohol. None of the strong acids seem to have any action on it.

Action of Sodic Methylate on Tribrom-trinitro-benzene.

Since sodic ethylate had acted so abnormally with tribrom-trinitro-benzene, it seemed of interest to study the action of sodic methylate on this compound, and accordingly we proceeded as follows.

10 grams of tribrom-trinitro-benzene in a flask were covered with absolute methyl alcohol, and the solution of sodic methylate made from 1.5 gram of sodium was added, observing the precautions for keeping the mixture cool described under the preparation of the corresponding ethyl compound. The first drop of sodic methylate solution turned red on touching the liquid in the flask, but this color faded to yellow as it was diffused through the solution; with continued addition of the methylate the color increased in intensity, becoming finally blood-red. It seemed as if the action of the sodic methylate was more vigorous than that of the ethylate, as after about three quarters of an hour the whole of the tribrom-trinitro-benzene had disappeared, leaving a clear red solution, but nevertheless the mixture was allowed to stand over night to make certain that the reaction had come to an end, after which the solvent was evaporated spontaneously, the residue washed with water (which gave a test for sodic nitrite), and crystallised from hot alcohol until it showed the constant melting-point 126°, when it was dried at about 70°, and analysed with the following results:

I. 0.2856 gram of the substance gave 10.1 cc. of nitrogen at a temperature of 25° and a pressure of 755.5 mm.

II. 0.2295 gram of the substance gave by the method of Carius 0.3072 gram of argentic bromide.

III. 0.2311 gram of the substance gave 0.3096 gram of argentic bromide.

	Calculated for $C_6Br_3NO_2(CH_3O)_3$.	Found. I.	II.	III.
Nitrogen	3.33	3.92	....	....
Bromine	57.15	...	56.97	57.03

Properties of Tribrom-nitro-resorcin Dimethyl-ether, $C_6Br_3NO_2(CH_3O)_2$.—This substance crystallises in white, flattened prisms terminated usually by a single plane at a very sharp angle to the sides; rarely, by two planes at an obtuse angle to each other; or also, rarely, the ends are square. It melts at 126°; and is nearly insoluble in cold water, perhaps a little more soluble in hot; only moderately soluble in ethyl alcohol even when hot, less soluble in it cold. It is much less soluble in alcohol than the corresponding ethyl compound; in this these two compounds resemble the methyl and ethyl compounds of the brom-dinitro-resorcin. Slightly soluble in cold methyl alcohol, more soluble in hot; freely soluble in benzene, chloroform, or acetone; soluble in ether, carbonic disulphide, or glacial acetic acid; very slightly soluble in ligroine. The three strong acids have no apparent action on it.

Action of Sodic Phenolate on Tribrom-trinitro-benzene.

After several unsuccessful experiments we obtained satisfactory results as follows: 10 grams of tribrom-trinitro-benzene were dissolved in a mixture of benzene and ordinary alcohol, and mixed with the sodic phenolate made from somewhat more than 6.1 grams of phenol treated with the sodic ethylate from 1.3 gram of sodium. The slight excess of phenol was used to avoid the presence of sodic ethylate, and the salt was added in suspension in alcohol. The mixture was then heated on the steam-bath under a return-condenser for less than five minutes, when it had turned bright green, but was perfectly clear, and upon cooling solidified, since it became filled with loose woolly masses of radiating needles looking like thistle-balls; this sudden solidification of the solution as it cools is very striking. The crystals with the residue from the mother-liquors were washed with water (which took up much sodic bromide), and crystallised from a mixture of alcohol and benzene until they showed the constant melting-point 175°, when they were dried at 100° and analysed. If benzene was not used in preparing this substance, the action was only incomplete, even after boiling for half an hour. The formation of sodic bromide instead of sodic nitrite, and the green instead of red color, showed that this action had gone differently from that with sodic ethylate or methylate, and this was confirmed by the following analyses:

I. 0.2689 gram of the substance gave on combustion 0.5823 gram of carbonic dioxide and 0.0850 gram of water.

II. 0.2439 gram of the substance gave 0.5306 gram of carbonic dioxide and 0.0775 gram of water.

III. 0.2448 gram of the substance gave 18.6 cc. of nitrogen at a temperature of 23° and a pressure of 758.1 mm.

	Calculated for $C_6(C_6H_5O)_3(NO_2)_3$.	Found. I.	II.	III.
Carbon	58.89	59.05	59.33	...
Hydrogen	3.07	3.51	3.53	...
Nitrogen	8.59	...	...	8.55

The substance was free from bromine. This action, therefore, has gone entirely differently from any of the others studied in this paper, consisting in the simple replacement of each bromine by one phenoxy radicle (C_6H_5O), and the substance is the trinitro-phloroglucine triphenyl-ether.

Properties of the Trinitro-phloroglucine Triphenyl-ether, $C_6(NO_2)_3(C_6H_5O)_3$.

This substance crystallises in long, very slender, white needles, matted together into globular, woolly masses which turn olive-brown on exposure to the air. It melts at 175°, and is essentially insoluble in water, whether cold or hot; slightly soluble in cold alcohol, more soluble in hot, but not freely; its solubility in methyl alcohol is similar to that in ethyl alcohol; very freely soluble in acetone or chloroform; freely soluble in benzene or glacial acetic acid; slightly soluble in ether or carbonic disulphide; very slightly soluble in ligroine. The three strong acids have no apparent action on it, whether hot or cold.

This is the only case in which we have observed the replacement of all three of the atoms of bromine by the radicle of an alcoholate, and it is to be noted that the phenoxy radicle introduced here is the most acid one which we have succeeded in introducing, whereas in the other cases where all the bromine has been replaced by the same radicle this has been the alkaline amido or anilido group,

$C_6(NH_2)_3(NO_2)_3$,[1] $C_6(NHC_6H_5)_3(NO_2)_3$,[2] $C_6H(NH_2)_2(NO_2)_2$,[3] $C_6H(NHC_6H_5)_2(NO_2)_2$.[4]

[1] This Journal **10**, 287. [2] Ibid. 290 [3] Ibid. **11**, 449. [4] Ibid. 455.

Experiments with Sodic Acetate, Sodic Picrate, or Sodic Nitro-methane on Tribrom-dinitro-benzene or Tribrom-trinitro-benzene.

In order to study the action of more acid radicles upon tribrom-dinitro-benzene, we mixed 5 grams of it with 3 grams of sodic acetate dissolved in dilute alcohol, and, as there seemed to be no action in the cold, heated the mixture in a flask with a return-condenser on the steam-bath for eight hours, at the end of which time the tribrom-dinitro-benzene was recovered unaltered, as indicated by its melting-point, 192°. A similar mixture was next heated at 100° for two days in a soda-water bottle closed with an india-rubber stopper, at the end of which time 4.9 grams of tribrom-dinitro-benzene, melting at 192°, were recovered. It is evident from these experiments that sodic acetate has no action on tribrom-dinitro-benzene at 100°.

As we hoped that the slighter acidity of picric acid might allow it to react on tribrom-dinitro-benzene, although sodic acetate would not, we next allowed 6.3 grams of tribrom-dinitro-benzene to stand for a week with 12 grams of sodic picrate suspended in alcohol, and, as at the end of this time no sodic bromide had been formed, we heated it in a flask with a return-condenser on the steam-bath for two days, but even after this no sodic bromide could be detected, and 6.2 grams of tribrom-dinitro-benzene, melting at 192°, were recovered in place of the 6.3 grams used. Sodic picrate, therefore, does not act on tribrom-dinitro-benzene at 100°.

In the hope that tribrom-trinitro-benzene would prove more reactive than the dinitro compound in this case, as it has in many others, the experiment was repeated with this substance, 5 grams of tribrom-trinitro-benzene to 8.3 grams of sodic picrate mixed with alcohol and benzene being used, but after twelve hours' boiling the 5 grams of the trinitro compound were recovered unaltered.

The sodium salt of nitro-methane was also tried with tribrom-dinitro-benzene. 10 grams of the latter substance dissolved in alcohol and benzene were mixed with 4.5 grams of nitro-methane previously treated with the sodic ethylate from 1.8 gram of sodium. The mixture, after standing for some time in the cold, became brownish-red, and the sodium salt suspended in the solution gradually disappeared, but upon working up the product 9.5 grams of the tribrom-dinitro-benzene were recovered unaltered, showing that there had been no action worth considering. In a

previous experiment another compound was obtained in small quantity, but we are inclined to ascribe its formation to sodic ethylate, or the products of the decomposition of the sodium salt of nitro-methane rather than to that substance itself. We hope to return to this subject next year.

We had intended to include in this research the action of sodic hydrate in alcoholic solution upon tribrom-dinitro-benzene; but since we obtained from a preliminary experiment brom-dinitro-resorcin diethyl-ether, recognised by its melting-point (182° instead of 184°, after one crystallisation) as the principal product, we thought the subject did not promise to be of sufficient interest to repay future work.

Some preliminary experiments with mononitro-tribrom-benzene and sodic ethylate seemed to promise interesting results, but this part of the work must be postponed until next year.

Action of Malonic Ester on Tribrom-dinitro-benzene.

In previous papers[1] of this series it has been proved that in the formation of brom-dinitro-phenyl-malonic ester from sodium malonic ester and tribrom-dinitro-benzene the bromine atom replaced by hydrogen stands between two nitro groups. In view of this fact, it seemed desirable to determine whether the ease with which this atom of bromine was removed by the action of malonic ester depended only on this position, and experiments were tried and described in a previous paper[2] which seemed to disprove this view. On returning to the subject, this point seemed to us of so much importance that we determined to repeat the experiment, especially as the conditions under which the malonic ester acted on the tribrom-dinitro-benzene in the earlier work were not exactly the same as those of the action of the sodium malonic ester in the preparation of brom-dinitro-phenyl-malonic ester; accordingly, in repeating the experiment as described below, we have reproduced these conditions as exactly as possible, except that malonic ester was used in place of sodium malonic ester.

To 4 grams of malonic ester dissolved in 30 cc. of absolute alcohol were added 5 grams of tribrom-dinitro-benzene dissolved in anhydrous benzene, and the mixture was allowed to stand in the cold for three or four days, at the end of which time, there being

[1] This Journal **11**, 556; **12**, 1. [2] Ibid. **12**, 309.

no signs that a reaction had taken place, the solvent was allowed to evaporate spontaneously, and the malonic ester mother-liquor poured off from the crystals, which, after careful drying on a steam radiator at about 70°, weighed 3.4 grams and melted at 192° (the melting-point of tribrom-dinitro-benzene). The mother-liquor was allowed to stand in a loosely covered dish for a month, when the malonic ester had evaporated, leaving an additional crop of crystals, which, after drying as before, weighed 1.75 gram, and also showed the melting-point of the tribrom-dinitro-benzene. So that the weight of the recovered tribrom-dinitro-benzene was 5.15 grams.[1] This experiment therefore confirms those previously tried,[2] and proves conclusively that malonic ester has no action upon tribrom-dinitro-benzene ($C_6BrNO_2BrNO_2BrH$), and, consequently, that the replacement of the bromine atom by hydrogen in the formation of brom-dinitro-phenyl-malonic ester depends on other conditions in addition to the influence of the nitro groups and other bromine atoms upon it. The discussion of these other conditions will be postponed until we have collected more experimental material.

SOME DERIVATIVES OF PHTHALIC SULPHINIDE.[3]

By C. W. Moulton.

Phthalic sulphinide was first obtained by Comstock,[4] and more carefully studied by Stokes,[5] who prepared several of its salts and ethers, and determined the constitution of its acid salts. The present work was undertaken with a view to studying the reactions involved in the preparation of this sulphinide and some of its derivatives.

The process employed was that recommended by Stokes, somewhat modified in certain details. It involves the following stages:

[1] The slight excess (0.15 gram) over the amount used is easily accounted for by the dust which during the long standing found its way into the loosely covered evaporating dish.

[2] This Journal **12**, 309.

[3] It gives me great pleasure to acknowledge my indebtedness to Professor Remsen for his guidance and assistance in this work, which was undertaken at his suggestion and carried on under his immediate supervision.

[4] This Journal **5**, 109. [5] Ibid. **6**, 262.

From naphthalene the α-naphthalene-sulphonic acid is made, and converted successively into the sodium salt, the sulphon-chloride, and the sulphon-amide. The oxidation of the latter by potassium permanganate in alkaline solution yields the sulphinide. Since the quantity of the latter hitherto obtained had been but a small percentage of the theoretical yield, an attempt was made to determine what are the conditions most favorable for the best results at each stage of the process.

The results of the experiments upon the preparation of the sulphinide may be summed up in the following directions:

One kilogram of finely-powdered naphthalene is thoroughly rubbed up with 750 grams of sulphuric acid in the cold. It is then heated over a water-bath until the naphthalene melts, and is kept at this temperature, with constant stirring, for two hours. The whole is poured into 12 liters of water at 85°, allowed to cool to 50°, filtered through cloth, neutralised with chalk, again filtered through cloth, and the calcium precipitated with sodium carbonate. It is once more filtered through cloth and evaporated down to two liters. On cooling, the salt which separates will be a nearly-pure sodium α-naphthalene-sulphonate. As much as possible of the mother-liquor is drawn off with a filter-pump, and the salt dried first at 110° and then at 185°, until water is no longer given off. The dry salt is powdered, and treated with 80 per cent. of its weight of phosphorus pentachloride, and, after heating on the water-bath to drive off the oxychloride, is cooled and washed once with cold water. The chloride is added in small portions to an excess of strong ammonia, and the mixture kept cool. The excess of ammonia is expelled by heating on the water-bath, and the sulphon-amide is washed by boiling in two or three liters of water, after which it is cooled, filtered out and dried. Of the amide, which is now sufficiently pure to oxidise, there should be about 450 grams. For the oxidation, 180 grams of crude caustic potash and 900 grams of potassium permanganate are dissolved in 12 liters of water, the solution heated to 40° and 200 grams of amide stirred in. The mixture is kept at a temperature between 60° and 100° until the permanganate is reduced; or for three hours, at the end of which time any remaining permanganate may be reduced with alcohol. After filtering through cloth and again through fluted filters, enough hydrochloric acid is added nearly to neutralise the alkali. The liquid is now evapo-

rated, *without boiling*, to one liter or less, and an excess of hydrochloric acid added, when upon cooling the acid potassium salt of the sulphinide separates out. This is dissolved in as much boiling water as may be necessary for solution, and recrystallised: a yield of 40–45 grams may be expected. Unless the manganese hydroxides are thoroughly washed, by boiling repeatedly in sufficient water, there will be a considerable loss, often more than 10 per cent. of the whole yield.

Conversion of the Acid Potassium Salt into the Free Sulphinide.

The salt thus obtained corresponded in appearance and properties with that described by Stokes. Since, according to this investigator, the potassium of this salt is acted upon very slowly by hydrochloric acid, he recommends the use of the silver salt from which to obtain the free sulphinide.

Upon boiling with *dilute* acid, however, more satisfactory results were obtained. 25 grams of crystallised acid potassium salt were dissolved in 450 cc. of water, and 50 cc. of concentrated hydrochloric acid (sp. gr., 1.175) added, and the whole boiled in a flask fitted with a reflux condenser. At the end of a half-hour the operation was suspended and the solution slowly evaporated to dryness. Upon recrystallisation from water, the product proved to be pure sulphinide, free from potassium chloride; but only 14 grams were obtained. To avoid so great a loss the experiment was repeated, as follows: 30 grams of the acid potassium salt were boiled with the same quantity of acid and water as before, for 15 minutes. The solution, treated as before, yielded 24 grams of sulphinide, and, as far as could be observed, was free from potassium chloride. When both the acid salt and the free sulphinide are present in a solution, if this be not too concentrated, on cooling, the much less soluble acid salt separates out first, although it may be subsequently obscured by the deposit of sulphinide. The crystalline form in which the acid salt first comes down from dilute solution is more characteristic than those described by Stokes. If the solution be of such a concentration that crystals begin to appear at about 50°, and the mother-liquor be poured off from the first-formed crystals while still hot, these crystals will appear at first sight to be steep rhombohedrons, but on closer examination more nearly resemble triclinic prisms terminated by basal planes. They are made up of thin plates parallel to the basal plane, and

on account of this structure no satisfactory measurements could be obtained.

Action of Hydrochloric Acid on Phthalic Sulphinide.

Remsen and Burton[1] have shown that benzoic sulphinide, on being boiled with dilute hydrochloric acid, is converted first into sulphamine-benzoic acid, and finally into the acid ammonium salt of sulpho-benzoic acid. Regarded as successive steps in hydration, these compounds are represented thus:

$$C_6H_4\begin{cases}SO_2\\CO\end{cases}>NH, \quad C_6H_4\begin{cases}SO_2.NH_2\\CO.OH\end{cases}, \quad C_6H_4\begin{cases}SO_3.NH_4\\CO.OH\end{cases}.$$

By analogy we should expect the same changes to take place in phthalic sulphinide, giving successively

$$C_6H_3\begin{cases}SO_2\\CO\\CO.OH\end{cases}>NH, \quad C_6H_3\begin{cases}SO_2.NH_2\\CO.OH\\CO.OH\end{cases}, \text{ and } C_6H_3\begin{cases}SO_3.NH_4\\CO.OH\\CO.OH\end{cases}.$$

In the preparation of phthalic sulphinide, as described above, the loss due to boiling indicating that similar decomposition does take place, experiments were conducted with a view to obtain, if possible, the corresponding sulphamine acid and the acid ammonium salt of sulpho-phthalic acid.

5 grams sulphinide in 250 cc. hydrochloric acid, diluted as above, were boiled for two hours in a flask fitted with a reflux condenser. The solution was evaporated to about 50 cc., and, upon cooling, the greater part of the sulphinide was deposited unchanged. After filtering, the mother-liquors stood for 48 hours and deposited, together with more sulphinide, some well-formed crystals which may have been the sulphamine acid; they were not obtained, however, in large enough quantity for purification and analysis. These crystals were prismatic in habit, short and thick, for the most part terminated by the basal plane only. The basal section was nearly hexagonal, apparently from a nearly equal development of the orthorhombic prism and macropinacoid.

From subsequent experiments with proportions similar to those given above, it was found that after ten hours' boiling the sulphinide is completely changed and the final product of the reaction is reached. That this was the acid ammonium salt of sulpho-phthalic acid could not be demonstrated by analysis. It is

[1] This Journal **11**, 404.

exceedingly soluble and, even when crystallised from absolute alcohol, in which it is quite easily soluble, it retains some of its impurities, and no satisfactory analysis could be obtained. The following facts, however, render it highly probable that the substance at hand was the acid ammonium salt:

1st. A solution of the crystallised substance was boiled a short time with an excess of barium carbonate, and a barium salt obtained which corresponded to the neutral barium salt of α-sulpho-phthalic acid as described by Comstock and again by Stokes. The salt, dried at 285° (the temperature applied by the latter investigator), gave upon analysis —

	Calculated for $\left(C_6H_3\begin{cases}SO_3\\CO_2\\CO_2\end{cases}\right)_2Ba_3$.	Found.
Ba	45.85 per cent.	45.60 per cent.

2d. A solution of the substance in absolute alcohol saturated with dry hydrochloric acid gave no ether of the sulphamine acid.

3d. On warming with caustic alkali ammonia was given off.

The analogy with benzoic sulphinide, which yields an acid ammonium salt under the same circumstances, leads to the same conclusion.

Action of Potassium Carbonate on Phthalic Sulphinide.

In evaporating the alkaline solution of the sulphinide, the loss on boiling indicated a breaking down of the ring under these conditions. To determine this point 3 grams of sulphinide were boiled with 10 grams of potassium carbonate in 200 cc. of water in a flask connected with a reflux condenser. On acidifying the solution after 10 hours' boiling, some acid potassium salt separated out. Another similar experiment gave, after 20 hours' boiling, no evidence of sulphinide on acidifying. An attempt to determine how far the hydration had gone under these circumstances was defeated by the difficulty of dealing with the products in the presence of so much inorganic matter, since they are exceedingly soluble in water and insoluble in ether.

The foregoing experiments show very conclusively that during the oxidation and subsequent concentration of the sulphinide, some loss must be expected if the solution be heated to boiling.

Ethers of α-Sulphamine-phthalic Acid.

When benzoic sulphinide in solution in alcohol is treated with dry hydrochloric acid, the sulphinide ring breaks down and an

ether of sulphamine-benzoic acid is formed, according to the expression

$$C_6H_4\begin{cases}SO_2\\CO\end{cases}>NH + ROH = C_6H_4\begin{cases}SO_2.NH_2\\CO_2R\end{cases}.$$[1]

In the case of phthalic sulphinide this reaction would be expected:

$$C_6H_3\begin{cases}SO_2\\CO\\CO_2H\end{cases}>NH + 2ROH = C_6H_3\begin{cases}SO_2.NH_2\\CO_2R\\CO_2R\end{cases} + H_2O.$$

This is in fact the reaction which takes place under these conditions. Unless, however, the sulphinide be dry and absolute alcohol be used, and the whole boiled for some time after saturation with hydrochloric acid gas, the reaction is not complete. The acid potassium salt of the sulphinide, dried at 185°, gives the most satisfactory results in making these ethers. 10 grams, finely powdered and suspended in 100 cc. of an alcohol, may be converted into the corresponding ether in three hours. The dimethyl, di-ethyl and di-propyl ethers were thus prepared. Their crystallising power and stability diminish with the increasing complexity of the alcoholic residue.

Di-methyl Ether of α-Sulphamine-phthalic Acid.

This dissolves quite readily in hot water and, on cooling, crystallises in long, narrow, exceedingly thin plates, which show a tendency toward radial grouping. When dried upon the filter the mass shows a very characteristic pearly lustre. It is more stable than the corresponding ethyl ether. After the second recrystallisation it showed no further change in the melting-point, which is 135°. Analysis for nitrogen gave the following results:

	Calculated for $C_6H_3\begin{cases}SO_2.NH_2\\CO_2.CH_3\\CO_2.CH_3\end{cases}$	Found.
N	5.14 per cent.	5.06 per cent.

Three determinations of sulphur made by Pearson's method gave, respectively, 10.76, 10.14 and 10.48 per cent., while theoretically there should be 11.74 per cent. of sulphur. In the last instance the greatest care was taken to secure complete oxidation, but apparently without success. Nevertheless it is not probable that the action with methyl alcohol differs from that with ethyl alcohol. The nitrogen analysis and the analogy with the ethyl

[1] Fahlberg and List: Ber. d. chem. Ges. **20**, 1601.

ether both point to the formula for this ether given above, while the wide divergence in these sulphur determinations tends to discredit them. A determination of the sulphur by Liebig's method gave the following results:

	Calculated for $C_6H_3\begin{cases}SO_2.NH_2\\CO_2.CH_3\\CO_2.CH_3\end{cases}$.	Found.
S	11.74 per cent.	11.89 per cent.

Di-ethyl Ether of α-Sulphamine-phthalic Acid.

This dissolves in water much less easily than the corresponding di-methyl ether. From concentrated solutions it separates out, on cooling, as an emulsion, which on standing clears up with the formation of long, needle-shaped crystals arranged in small bundles, the individuals in each bundle lying parallel to one another. From less concentrated solutions it crystallises, directly on cooling, in a characteristic coral-like formation of crystals radially grouped, the extremity of each becoming a centre for another tuft of needles. Their melting-point is 101.5°–102°. Analysis of this ether gave the following results:

	Calculated for $C_6H_3\begin{cases}SO_2.NH_2\\CO_2.C_2H_5\\CO_2.C_2H_5\end{cases}$.	Found.
N	4.66 per cent.	4.58 per cent.
S	10.64 "	10.15 " 10.36 "

Di-propyl Ether of α-Sulphamine-phthalic Acid.

This ether was made in the same manner as the compound last described. It can be crystallised only with great difficulty, and then but in part, the remainder settling to the bottom as an oil. A quantity sufficient for analysis was not obtained in crystalline form. Although a number of attempts were made, crystals were obtained but twice. These showed melting-points of 64° and 68° respectively. I had reason to believe that the sample showing the higher melting-point was more nearly pure. The crystals were in no case well formed, and the crystallising power of the ether is very weak.

It is interesting to note that in these ethers the effect of the increasing complexity of the paraffin residue is to lower the melting-point, and by an approximately constant difference,—

Di-methyl ether, ...	135°
Di-ethyl ether, ...	102°
Di-propyl ether, ...	68°

Action of Ammonia on the Di-ethyl Ether.

From the action of ammonia upon ethereal salts in general we should expect the following reaction:

$$C_6H_2\begin{cases}SO_2.NH_2\\CO_2.C_2H_5\\CO_2.C_2H_5\end{cases}+2NH_3=C_6H_2\begin{cases}SO_2.NH_2\\CO.NH_2\\CO.NH_2\end{cases}+2C_2H_5OH.$$

The ethyl ether was treated with an excess of strong ammonia in the cold, and allowed to stand 24 hours. It was then heated on the water-bath until no further odor of ammonia was given off, and, finally, was concentrated to a thin syrup, which on cooling was almost filled with crystals. These were recrystallised, and analysed for nitrogen with the following result:

	Calculated for $C_6H_2\begin{cases}SO_2.NH_2\\CO.NH_2\\CO.NH_2\end{cases}$ or $C_6H_2\begin{cases}SO_2\\CO\\CO.NH_2\end{cases}>N.NH_4$.	Found.
N	17.32 per cent.	17.67 per cent.

Some of this crystallised product, dissolved in water and acidified, gave a precipitate of pure carbamine sulphinide.

Carbamine Sulphinide.

Carbamine sulphinide is somewhat more soluble in cold, and less in hot, water than the acid potassium salt of the sulphinide. It is slightly soluble in strong, boiling alcohol, and insoluble in ether. It melts at 275° (uncor.).

The crystals first formed in the hot solution, as described above in the case of the acid potassium salt of phthalic sulphinide, somewhat resemble those of the latter salt, but with apparently less inclination of the axes. The general habit of the crystals when allowed to grow undisturbed, is quite different from that of the acid potassium salt, and closely resembles that of benzoic sulphinide. The development is tabular and lozenge-shaped, with an irregular growth-line along the longer diagonal.

Analysis of the carbamine sulphinide gave the following results:

	Calculated for $C_6H_2\begin{cases}SO_2>NH\\CO\\CO.NH_2\end{cases}$.	Found.
N	12.42 per cent.	12.33 per cent. 12.15 "
S	14.17 "	14.38 "

Analysis of its salts confirmed these results.

Whether the ring was reformed by the action of the ammonia —the triamide losing one molecule of ammonia, and then taking it up again to form a salt; in which case the stages of the reaction would be represented thus:

$$C_6H_3\begin{cases}SO_2.NH_2\\CO.NH_2\\CO.NH_2\end{cases},\quad C_6H_3\begin{cases}SO_2\\CO\\CO.NH_2\end{cases}>NH,\quad C_6H_3\begin{cases}SO_2\\CO\\CO.NH_2\end{cases}>N.NH_4;$$

or whether the action of the hydrochloric acid was necessary to reform the ring; was not determined. The former is the more probable supposition.

Three salts of the carbamine sulphinide were obtained:—

Ammonium salt of carbamine sulphinide.—The product of the action of ammonia upon the di-ethyl ether, as described above, was regarded as this ammonium salt—a conclusion drawn from the analysis and from the action of hydrochloric acid upon the compound. It is exceedingly soluble in water, from which it crystallises in fine, nearly-rectangular needles—apparently orthorhombic prisms terminated by dome faces of one form only.

Barium salt of carbamine sulphinide.—This separated as a crystalline precipitate, upon concentrating a solution of the carbamine sulphanide which had been boiled with barium carbonate. Its solubility in hot and in cold water were too nearly alike to render its purification by recrystallisation practicable with the small amount at hand. It was therefore dried to constant weight at 110°, and analysed for barium as follows:

	Found.
Ba	25.00 per cent.

From the following calculated values it will be seen that this corresponds more closely to the amount contained in the barium salt of the monobasic acid $C_6H_3\begin{cases}SO_2\\CO\\CO.NH_2\end{cases}>NH$:

	Calculated for $C_6H_3\begin{cases}SO_2\\CO\\CO.NH_2\end{cases}>NBa_{\frac{1}{2}}$.	$C_6H_3\begin{cases}SO_2\\CO\\CO_2\end{cases}>N>Ba$.	$C_6H_3\begin{cases}SO_2.NH_2\\CO_2\\CO_2\end{cases}Ba$.
Ba	23.35 per cent.	37.87 per cent.	36.07 per cent.

Silver salt of carbamine sulphinide.—A hot, concentrated solution of carbamine sulphinide was treated with an excess of silver nitrate. Almost immediately a crystalline salt began to separate out. The crystals were not very sharply formed, but had a characteristic habit. Those especially which formed upon the side of

the beaker were 2 to 3 mm. in length, and appeared to be orthorhombic prisms terminated at both ends by steep brachydome faces so developed that the corresponding upper and lower planes nearly met. This salt is soluble in water only with great difficulty; 0.26 gram could not by prolonged boiling be brought completely into solution in a half-liter of water. The salt was analysed without recrystallising. Air-dried it gave 31.90 per cent. of silver; calculated for the silver salt of carbamine sulphinide, without water, 32.40 per cent.

As was afterwards shown, these unsatisfactory results were due to the fact that carbamine sulphinide is decomposed by boiling in water, yielding phthalic sulphinide. The presence of salts of the latter compound with those of carbamine sulphinide prepared as above, was therefore to be expected.

α-Sulpho-phthalic Acid.

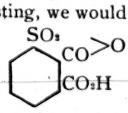
Salts of this acid have been described by Comstock and by Stokes. The free acid has not before been prepared.

The acid ammonium salt described above, obtained by the action of dilute hydrochloric acid upon phthalic sulphinide, was mixed with an excess of phosphorus pentachloride. In most cases no action was perceptible until the mixture was quite strongly heated. The resulting chloride was washed in cold water. An attempt to crystallise this chloride failed. Some of the washed product, dried over phosphorus pentoxide and dissolved in absolute ether, remained as an oily mass after the evaporation of the ether. The chloride melts under water below the boiling-point, and is slowly decomposed by boiling water. It may be washed, with little loss, by boiling in water a short time. When boiled with water for two hours it is completely converted into the acid, which was identified by making the gelatinous silver salt described by Stokes, and also by the barium salt. It is extremely soluble in water, and quite easily soluble in absolute alcohol, but not at all in ether. If its aqueous solution be evaporated down to a thin syrup it becomes a solid mass of crystals when cold. By pouring off the mother-liquors before they were quite cold, crystals were obtained whose planes were not well formed, probably because of the rapidity of formation in so viscous a mass; for the substance has strong crystallising powers, and a drop of a somewhat more dilute solution leaves, upon evaporating, a bunch of radiating needles. The best formed crystals were apparently triclinic,

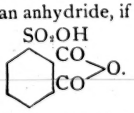
columnar in habit, with a development of the fundamental prism and macropinacoid, terminated by the basal plane. They melt in the water which clings to them, below 35°. Dried over night in a press between filter papers, they melt at 62°–64°. On standing exposed to the air for a few days they become opaque. An attempt to determine the water of crystallisation was unsatisfactory. Some of the acid, dried as above, was heated for 5 hours below 100°, but no constant weight was reached. It was then heated several hours longer below 120°, until the loss of weight nearly ceased, the loss being very slow during the last hour. The entire loss was 19.75 per cent. of the acid taken, corresponding more nearly to four molecules (22.64 per cent.) of water of crystallisation. Even below 100° the acid blackened somewhat; and when the operation was discontinued, was blackened nearly throughout. On attempting to redissolve in water, the greater part passed readily into solution, but enough black insoluble matter remained to indicate that a decomposition had taken place to some extent.

Attempt to Prepare an Anhydride of Sulpho-phthalic Acid.

Remsen and Dohme[1] have shown that ortho-sulpho-benzoic acid gives, when sublimed with phosphorus pentoxide, an anhydride which has the formula $C_6H_4\begin{cases}SO_2\\CO\end{cases}>O$. The ease with which phthalic anhydride is obtained is well known. Since, then, in *a*-sulpho-phthalic acid both these relations are regarded as existing, we would look for the formation of an anhydride, if not



, at least might we expect



Some of the sulpho-phthalic acid, dried for a month over sulphuric acid, and having apparently lost all its water of crystallisation, was mixed with phosphorus pentoxide and heated by means of a sulphuric acid bath, in a small flask provided with a cooling tube. After several hours' heating at 175° there was no evidence of sublimation. A sand bath was substituted for the acid bath, and the heat gradually increased until the mass within was blackened, but no sublimate was obtained.

Chemical Laboratory, Johns Hopkins University.

[1] This Journal **11**, 334.

THE ACTION OF AN ALCOHOLIC SOLUTION OF SILVER NITRATE ON THE ETHYL ETHER OF PHENYL-DIBROM-PROPIONIC ACID.

By Leonard P. Kinnicutt and George D. Moore.

In a paper on the action of alcoholic solutions of silver nitrate on aromatic compounds containing bromine in the side-chain, it was shown that its action on the ethyl ether of phenyl-dibrom-propionic acid was to remove one half of the bromine.[1] The substance formed was not at that time isolated; this we have now done, and find that it is the ethyl ether of phenyl-α-brom-β-nitro-propionic acid.

If the ethyl ether of phenyl-dibrom-propionic acid is dissolved in boiling alcohol, and silver nitrate dissolved in alcohol is added in amounts equalling one, two or three molecules, a precipitation of bromide of silver immediately takes place, and at the end of an hour, the solution being shaken from time to time, this precipitate settles, leaving a perfectly clear solution. The amount of silver bromide obtained, whether one, two or three molecules of silver nitrate were used, was that which would be given by the removal of one atom of bromine from the ether.

On pouring the clear alcoholic solution into water an oil separates out, which can be separated from the water by shaking with ether. The oil so obtained, after being dried over calcium chloride, gave on analysis an amount of bromine corresponding to that required by the ethyl ether of phenyl-monobrom-mononitro-propionic acid. Three separate preparations of the oil, using different amounts of silver nitrate, gave the following percentages of bromine: 26.32, 26.42, 26.46.

Theory for $C_6H_5CHNO_2CHBrCOOC_2H_5$, 26.48.

The oil is of a pale straw color, with a sweetish odor, soluble in alcohol and ether.

Distilled in vacuum, 20 mm., it begins to boil at 85°, hydrobromic acid being given off. The temperature slowly rises to 180°, at which point all the oil distills over. After washing the distillate to remove the hydrobromic acid, and redistilling in vacuum, 20 mm. pressure, the oil begins to boil at 75°, hydro-

[1] Kinnicutt and Sweetser: This Journal 6, 415.

bromic acid again being given off. About one fourth of the oil distills over between 75° and 85°, the temperature then rises rapidly to 165°, the main portion of the oil distilling between 165° and 175°. The portion of the oil distilling between 75° and 85° has the odor, the boiling-point, and reaction with ammonia of benzoic aldehyde. The oil distilling between 165° and 175° still contains both nitrogen and bromine. On oxidation the substance yields benzoic aldehyde, and on treatment with sodium hydrate the monobrom-cinnamic acid which melts at 131° is formed. These reactions indicate that the nitro group must have the β position.

On heating the substance for a long time with an excess of an alcoholic solution of silver nitrate, slow decomposition takes place. Fifteen grams of the substance were treated with fifteen grams of silver nitrate dissolved in alcohol, placed in a flask connected with an inverted cooler, and heated over a water-bath. At the end of ten hours one-half gram of silver bromide was precipitated; this amount gradually diminished till at the end of two weeks no further reaction seemed to take place. The oil that was thus obtained contained about 16 per cent. of bromine, and from its odor benzoic aldehyde seemed to be present.

A further study of the nitro compound, and also the study of the products formed by the action of silver nitrate on various paraffin as well as aromatic bromine compounds, is now being carried on in the laboratory.

Kinnicutt and Sweetser[1] have already shown that nitrate of silver easily removes all the bromine from phenyl-β-brom-propionic acid, while it has no action on either of the two isomeric monobrom-cinnamic acids. This is easily explained by ascribing to these two acids the formula recently given to them by Erlenmeyer,[2] and we hope the results of further work with silver nitrate will show that the position of bromine atoms in the side-chain can be determined by the use of this reagent.

WORCESTER POLYTECHNIC INSTITUTE.

[1] This Journal **6**, 416.

[2] Ber. d. chem. Gesell. **23**, 3130.

THE ELECTROLYSIS OF METALLIC PHOSPHATES IN ACID SOLUTION.

By Edgar F. Smith.

In a former article,[1] bearing the above title, I showed that copper and cadmium could be precipitated electrolytically from solutions of their phosphates. Their separation from each other was also noted, as well as the separation of the individual metals from iron, aluminium, chromium, zinc, nickel, and cobalt. Further, the separation of copper from manganese was shown to answer all practical requirements. The free phosphoric acid, present in the solution, prevented the deposition of the manganese as dioxide.

Since reporting this last separation I have found that cadmium can be separated from manganese electrolytically without any particular difficulty.

Cadmium from Manganese.

When I electrolysed the acid phosphates of copper and manganese, 10 cc. of phosphoric acid (sp. gr., 1.347) were present in the solution. The current employed gave 0.10 cc. OH gas per minute. In the presence of such a large excess of acid, cadmium was not precipitated by a current yielding 10 cc. OH gas per minute. It therefore became necessary to know just what quantity of free acid could be present in the solution and the cadmium be entirely deposited. The quantity of acid requisite for the retention of the manganese was of importance. Several trials led to the following conditions as being best suited for the complete separation of the metals under discussion:

1. 10 cc. cadmium sulphate solution (=0.2399 gram cadmium), 10 cc. manganese sulphate solution (=0.1000 gram manganese), 20 cc. disodium phosphate (sp. gr., 1.0358), 3 cc. phosphoric acid (sp. gr., 1.347), and 100 cc. water were electrolysed with a current liberating 10 cc. OH gas per minute. In twelve hours 0.2394 gram cadmium was precipitated. Not the slightest deposition of manganese dioxide was observed upon the anode.

2. In this trial the conditions were precisely the same as those given in 1. The deposit of cadmium metal weighed 0.2400 gram.

It will be noticed that the error in the results is fully within the limit. Cadmium was not detected in the filtrate.

[1] This Journal **12**, 329.

The deposits in both experiments were very crystalline. Hot water was employed in washing the metal. The drying was done upon a warm iron plate. The current was invariably increased for about an hour before its final interruption. The acid liquid was siphoned off from the metallic deposit before the vessel in which the precipitation occurred was disconnected.

Some of the heavier metals were studied in the same manner as copper and cadmium. The results of this study are given below. They are new and have value for the student of electrolysis.

Platinum.

0.2590 gram of ammonio-platinum chloride was dissolved in water. To this solution I added 30 cc. disodium phosphate (sp. gr., 1.0358), 5 cc. phosphoric acid, and diluted with water to 150 cc. A current liberating 0.8 cc. OH gas per minute acted upon the solution for a period of ten hours. The precipitated platinum metal was quite adherent. It was washed with water and alcohol. It weighed 0.1140 gram. The calculated amount of platinum corresponding to the quantity of double salt used in the trial is 0.1144 gram. The error is therefore 0.0004 gram.

Two additional trials gave 0.1255 gram and 0.1263 gram metal. The required quantity of platinum was 0.1260 gram.

The filtrates from these deposits were not discolored upon the addition of hydrogen sulphide. The precipitated metal was deposited upon a copper-coated platinum surface.

A current best suited for the precipitation of 0.1–0.2 gram metallic platinum should give about 0.4 cc. oxyhydrogen gas per minute. If the current exceeds 0.7–0.8 cc. OH gas per minute, the platinum is apt to separate in a spongy condition, and when the current falls as low as 0.2 cc. OH gas per minute, the copper coating dissolves.

Platinum is deposited very rapidly from its acid phosphate solution by the current.

The conditions outlined above allow of the electrolytic separation of platinum from the metals of the third and fourth groups.

Palladium.

This metal, under the influence of the current, separates very rapidly from a solution containing free phosphoric acid. The deposition is also complete.

1. A solution containing 0.1825 gram palladium, 20 cc. disodium phosphate (sp. gr., 1.0358), 5 cc. phosphoric acid (sp. gr., 1.347), and 125 cc. of water was electrolysed with a current giving 0.7 cc. OH gas per minute. The deposited metal weighed 0.1817 gram. It was washed with hot water. The deposition was made upon a copper-coated platinum dish.

2. The conditions of experiment were analogous to those in 1. The precipitated platinum weighed 0.1830 gram.

In each instance the deposit of metal was compact and adherent. It resembled ordinary sheet palladium in appearance after it was dried.

The efforts made to separate palladium from cadmium, zinc and other metals were fruitless. The palladium was always fully precipitated, but it either carried down with it as much as three per cent. of the associated metal, or it separated in spongy, black masses. For the present the acid phosphate solution of palladium can only be recommended for electrolysis when other metals are not present with the palladium.

Gold.

1. The solution contained 0.1338 gram gold, 20 cc. disodium phosphate (sp. gr., 1.038), and 3 cc. phosphoric acid (sp. gr., 1.347). Total dilution, 160 cc. Current, 0.8 cc. OH gas per minute. The metal was deposited upon copper. The deposit weighed 0.1335 gram. The filtrate was found free from gold.

The metallic deposit was quite adherent and compact. It was washed with hot water.

2. The conditions were similar to those just mentioned under 1. The gold deposit weighed 0.1339 gram.

Trials made for the purpose of separating gold from cadmium were not successful. The same behavior was observed here as with palladium and cadmium. The gold separated completely from the solution, but it either carried down cadmium or it separated in a spongy mass. This last occurrence was always noticed when the quantity of phosphoric acid was increased.

I failed to separate palladium from zinc, notwithstanding the conditions were repeatedly modified. With gold and zinc the separation proceeded without the least difficulty.

Gold from Zinc.

A solution of 150 cc. volume contained 0.1338 gram gold, 0.1500 gram zinc, 30 cc. disodium phosphate (sp. gr., 1.0358), and 3 cc. phosphoric acid. It was electrolysed with a current giving 0.6 cc. OH gas per minute. The gold deposit was compact, and readily washed with hot water. It was dried over a warm iron plate. It weighed 0.1338 gram. Zinc was not precipitated.

Gold from Cobalt.

The quantity of metallic gold present was the same as in the preceding separation. The metallic cobalt was 0.2300 gram. The conditions, in all other respects, were the same as in the separation of gold from zinc. The precipitated gold weighed 0.1338 gram.

The current employed in the experiments recorded in this communication was derived from the "crowfoot" cells of the ordinary form. The flat platinum spiral in connection with the anode of the battery was 1¾ inches from the cathode dish, in which the depositions of metal were made. All the precipitations occurred at the ordinary temperature.

The electrolysis of zinc, nickel, cobalt and iron phosphates, in acid solution, has thus far not yielded very encouraging results. Strong currents seem necessary. Even then the deposition of the metals is rather slow.

UNIVERSITY OF PENNSYLVANIA, *January* 10, 1891.

REVIEWS AND REPORTS.

HYDRAZINE HYDRATE AND THE DIAMMONIUM HALOGEN SALTS.

Two years ago a paper by Curtius and Jay[1] announced the fact of the isolation of hydrazine. Another paper in the same series has recently appeared,[2] in this case by Curtius and Schulz,

[1] J. prakt. Chem. [2] **39**, 27. An abstract of this paper will be found in This Journal **11**, 149.
[2] J. prakt. Chem. [2] **42**, 521.

which deals with the constitution of hydrazine hydrate and the hydrazine halogen salts.

From the sulphate, $N_2H_4.H_2SO_4$, prepared as described in the former paper, hydrazine hydrate is obtained when the salt is heated in a silver distilling-apparatus with caustic potash. The distilled hydrate was analysed, one of the methods used being based upon the reaction which takes place when platinum chloride in acid solution is treated with this base,—platinous chloride is formed and nitrogen is given off:

$$2PtCl_4 + N_2H_4.H_2O = 2PtCl_2 + 4HCl + N_2 + H_2O.$$

The nitrogen was collected and measured in an apparatus designed for the purpose. The analyses show that the composition of the hydrate is to be represented by the formula $N_2H_4.H_2O$. Numerous molecular weight determinations were made both by the vapor-density methods of Hofmann and Victor Meyer, and by the method of Raoult. These show (1) that in aqueous solution the hydrate has the composition represented by the formula $N_2H_4.2H_2O$; that at 100° and *in vacuo* the vapor density corresponds to a molecular weight of 50 ($N_2H_4.H_2O = 50$); that at 170° under ordinary pressure the density is only one half as great—showing, apparently, complete dissociation into hydrazine and water; and that above 170° the density increases again, until at the temperature of the lead-bath it appears to correspond to a molecular weight of 100!

Some of the properties of the hydrate have already been given.[1] In addition the following may be of interest: It is hygroscopic and attracts carbon dioxide from the air. It mixes with water and with alcohol in all proportions, but not with ether, chloroform or benzene. It will solidify in a mixture of solid carbon dioxide and ether. The specific gravity of the substance is 1.03 at 21°; its boiling-point is 118.5° under a pressure of 739.5 mm. It reacts in a marked manner with (red) litmus- and turmeric-paper.

As soon as the attempt is made to isolate hydrazine from the hydrate serious difficulties are at once encountered. If, for example, the hydrate is allowed to drop upon powdered barium oxide, great heat is generated, but, on raising the temperature for the purpose of distilling off the hydrazine, the *hydrate* passes over unchanged. Repeated distillation over barium oxide does, however, abstract a little of the water, and as a result the liquid fumes strongly in the air. Since at 170° there is apparently complete dissociation into water and hydrazine, some of the hydrate was heated to that temperature in the presence of barium oxide in a closed tube. On opening the tube, hydrazine escaped in the form of white fumes characterised by an intense odor. Further work will be done upon the base thus isolated.

[1] This Journal **11**, 142.

The following halogen salts are described:

I.	$N_2H_4.2HF$,	$N_2H_4.2HCl$,	$N_2H_4.2HBr$,	$N_2H_4.2HI$.
II.	...	$N_2H_4.HCl$,	$N_2H_4.HBr$,	$N_2H_4.HI$.
III.	...	...	...	$(N_2H_4)_2.2HI$.

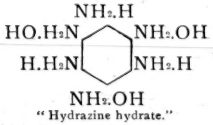
These salts exhibit in an interesting way the gradation in the properties of the halogen acids. For it will be seen that but one fluorine compound is known, and that the one containing the largest proportion of acid. Of the chlorine compounds, that belonging to the first class is prepared with ease by a number of methods; the second is obtained indirectly—by heating the more acid salt. Of the bromine compounds, that belonging to the second class is obtained with less difficulty than the other. Finally, of the hydriodic acid salts, the first is prepared only with considerable difficulty, the second—*and third*—with ease; no salt corresponding to the last but containing another halogen is known. Molecular weight determinations by Raoult's method were made for all these salts.

Among the reactions of these salts the following facts are to be noted: 1. The trihydrazine dihydriodate passes over with ease, on treatment with hydriodic acid, into "diammonium monoiodide"—$(N_2H_4)_3.2HI + HI = 3(N_2H_4.HI)$; and 2. It is only with considerable difficulty that this "monoiodide" can be transformed into the "diiodide," $N_2H_4.2HI$.

Taking these facts, together with the composition of the hydrate and salts, into consideration, the authors come to the conclusion that the only formulæ which will serve to represent the constitution of the derivatives of hydrazine belonging to the second and third classes, as given above, are of this kind:

I.

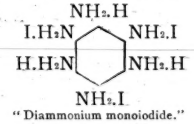
$3(N_2H_4.H_2O)$,
Trihydrazine trihydrate.



"Hydrazine hydrate."

II.

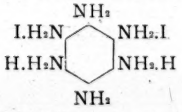
$3(N_2H_4.HI)$,
Trihydrazine trihydriodate.



"Diammonium monoiodide."

III.

$(N_2H_4)_2.2HI = N_6H_{12}.2HI$,
Trihydrazine dihydriodate.



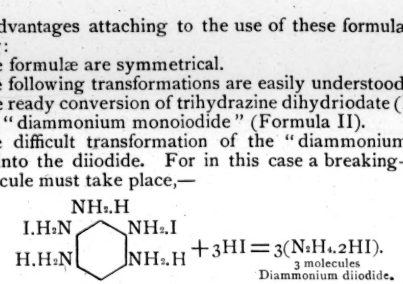
The advantages attaching to the use of these formulæ are the following:

1. The formulæ are symmetrical.

2. The following transformations are easily understood:

a. The ready conversion of trihydrazine dihydriodate (Formula III) into "diammonium monoiodide" (Formula II).

b. The difficult transformation of the "diammonium monoiodide" into the diiodide. For in this case a breaking-down of the molecule must take place,—



3. The existence and stability of the mono-hydrate and the mono-halogen salts is easily explained; the formulæ represent saturated molecules.

WYATT W. RANDALL.

THE ELEMENTS OF QUALITATIVE ANALYSIS. By W. A. NOYES, Ph. D., Professor of Chemistry in the Rose Polytechnic Institute. Second Edition, revised. Holt & Co.: New York, 1890. 91 pp.

The author gives two reasons which have led to the writing of this book. "One has been the desire to give to my classes a scheme for qualitative analysis in which points where a beginner is liable to make mistakes are especially guarded by careful and explicit directions for procedure." "The second reason . . . has been the desire to connect the reactions given by way of a study of the elements before actual analysis more closely with the cause of analysis itself." Both reasons are good ones. The book shows that it has been prepared with unusual care by one well qualified for the work, and it can be recommended to those looking for a guide to qualitative analysis for use in large classes.

I. R.

ELECTRO-CHEMICAL ANALYSIS. By EDGAR F. SMITH, Professor of Analytical Chemistry, University of Pennsylvania. Blakiston, Son & Co., Philadelphia, 1890. 116 pp. 12mo.

Chemists will find this little book an excellent guide to a knowledge of the methods of quantitative analysis by electrolysis. As the author has himself contributed not a little to our knowledge of these methods, he is specially prepared for a work of this kind. The first part of the book treats of matters electrical,

such as Electrical Units, Sources of Electrical Currents, Reduction of the Current, Measuring Currents, etc. The special part then deals with the Determinations of Metals, Separation of Metals, and Oxidation by means of the Electric Current. In the case of each metal references are given to the original articles. The descriptions of the individual methods are sufficiently detailed to enable the student to follow them without difficulty. I. R.

ANLEITUNG ZUR DARSTELLUNG CHEMISCHER PRAEPARATE. Ein Leitfaden für den praktischen Unterricht in der unorganischen Chemie. Von Dr. HUGO ERDMANN. Frankfurt a. M.: Verlag von H. Bechholz. 1891.

This book aims to be for laboratory work in inorganic chemistry what the books of Fischer and Levy are for work in organic chemistry. It gives full directions for making nearly one hundred preparations, so chosen as to include derivatives of all the common elements. In the selection particular attention is given to the anhydrous chlorides, which, as the author says, test the ability of the student to work neatly and carefully. The author is Privatdocent at Halle, and has acted as laboratory assistant to Prof. Volhard for several years, during which time the methods here given were in constant use in the regular course of instruction, and were thoroughly tested. The book is good and really fills a gap in the list of laboratory handbooks. It can be recommended to students, and should certainly have a place in the library of every laboratory. E. R.

NOTES.

Osmotic Pressure.

In the Zeitschr. f. Phys. Chem. **6**, 474, Prof. Boltzmann of Munich has a most interesting paper on osmotic pressure from a theoretical point of view. He considers the case of a dilute salt solution enclosed in a vessel with a "semi-permeable" diaphragm, and shows (*by simple mechanical principles*) that, when there is equilibrium, there must be a pressure exerted on the diaphragm, as a result of the actions of the salt-molecules and the solvent itself. If the temperature is the same, this pressure is identical with that which the same number of gaseous molecules occupying the same space as the solution would produce, provided only that

the mean kinetic energy of the two systems of particles is the same. The author discusses briefly cases of diffusion, electrolysis, etc., and by known laws and simple hypotheses arrives at the equations deduced by Arrhenius, Planck, Nernst and others.

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